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ERRATA:

ERRATA in Vol. 62, 1937:—

p. 88. The Enzymes of Milk. Delete the tenth line of paragraph (v) and substitute: "are ground intimately together in a mortar, and 0·1 g. of the mixed dye is dissolved in 1 litre of water. For use, 10 ml. of this stock solution. . . ."

p. 323. Last abstract. *For* "J. M. Skimwell" *read* "J. L. Shimwell."

p. 404. First abstract. *For* "I. L. Shinwell" *read* "J. L. Shimwell."

p. 671. 3rd line from bottom. In the sentence "toxins produced by members of the food-poisoning or dysentery groups" *omit* "toxins produced by."

p. 753. 3rd line, *for* "50 to 90 bacteria per gram" *read* "50 to 90 millions."

,, 5th line, *for* "both" *read* "broth."

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held on Wednesday, December 2nd, 1936, at the Chemical Society's Rooms, Burlington House, the President, Dr. G. Roche Lynch, in the chair.

Certificates were read in favour of:—Granville Hubert Clarke, Leonard Cartlidge Dutton, A.I.C., John Charles Giblin, B.Sc., A.I.C., Ronald William Gillham, Ph.C., Ronald Murray Hamilton, Walter Thomas Lunt, B.Sc., A.I.C., William Douglas McFarlane, M.A., Ph.D., William Stewart Patterson, Ph.D., M.Sc., F.I.C., Thomas Charles Williams, B.Sc., A.I.C., George Henry Wray.

The following were elected members of the Society:—Frederick Brown, Alan James Cavell, A.R.C.S., D.I.C., A.I.C., James Pettigrew Ogilvie, F.I.C., Richard Kenneth Sanders, B.A., Alexander Martin Smith, Ph.D., D.Sc., A.I.C., George Edward Speight, A.Met., B.Sc.

The following were elected Honorary Members of the Society:—Bernard Cracroft Aston, F.I.C., and Robert Howson Pickard, D.Sc., Ph.D., F.I.C., F.R.S.

The following papers were read and discussed:—"The Detection of Arachis Oil in Olive Oil," by Norman Evers, B.Sc., F.I.C.; "The Enzymes of Milk, I, Notes on Kay and Graham's Phosphatase Test," by E. B. Anderson, M.Sc., F.I.C., Z. Herschdorfer, Ph.D., and F. K. Neave; "The Determination of Cyanide in Aqueous Extracts of Road Tars," by W. G. Moffitt, Ph.D., A.I.C., and E. H. Williams, B.Sc., A.I.C.; and "A Rapid Method for the Determination of Triethanolamine," by C. J. Eastland, F.I.C., Norman Evers, B.Sc., F.I.C., and T. F. West, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Manchester on December 12th. There was an attendance of twenty-nine; in the absence of the Chairman and Vice-Chairman, Prof. W. H. Roberts was elected to the chair.

The following paper was read and discussed:—"Sussex Ground Oats," by F. Robertson Dodd, F.I.C., and A. Pattinson Telford.

A discussion took place on the desirability of changing the title of the parent Society.

SCOTTISH SECTION

An ordinary meeting of the Section was held in the Central Hotel, Glasgow, on November 19th, 1936.

Professor G. G. Henderson gave a short informal address, and the following papers were read and discussed:—"Note on the Estimation of Lead in Drinking Water," by J. W. Hawley, B.Sc., F.I.C., and W. Wilson, F.I.C.; and "The Analysis of Peaty Waters," by R. T. Thomson, F.I.C.

Obituary

JOHN MAY HERBERT MUNRO

By the passing of Dr. Munro on November 6th, 1936, those who knew him have lost a great friend, and the Society of Public Analysts one of its oldest members.

John May Herbert Munro was born on December 23rd, 1854, at Kingswood, near Bristol. He was educated first at a preparatory school in Painswick, then at Taunton School, and later attended the Trades School, Bristol, where he had his life-long friend, Sir Ernest Cook, as his fellow pupil.

In those days it was the policy to encourage the study of science by offering Science Exhibitions for competition among the schools of the country. In the examination of 1872 there were only six Exhibitions available, and although Munro did not secure one of them, he was so nearly successful that he was offered a modified Exhibition, which enabled him to enter the Royal College of Science, Dublin. After the usual three-year course, he took the Associateship of the College, and in 1876 returned as an assistant master to his old school in Bristol, and, while there, he took his D.Sc. at London University. He next competed for, and obtained, an examinership in the Patent Office, London, where he remained until 1880, when he joined Messrs. Wrightson and Fream in founding the Agricultural College at Downton.

It was not until middle life that he turned his attention to medicine—in fact, he was still a professor at Downton while taking the preliminary medical course at Bristol University.

Dr. Munro, who had been elected a Fellow of the Institute of Chemistry in 1888, was appointed Agricultural Analyst to the Wiltshire County Council in 1897; he was also Agricultural Analyst to the City of Bath, and held both appointments until his death. From 1925 to 1928 he was Honorary Analyst to the Baths Committee at Bath.

He published the results of a number of investigations on the biochemical aspects of medical problems (cf. *Lancet*, December 3rd, 1932, p. 1211).

Although he had a great gift of imparting knowledge and was a born teacher, yet he himself never ceased to be a student. He was quiet and reserved in his manner, but, when once drawn into conversation, he held the interest of his listeners. His unfailing kindness and understanding endeared him to his patients, many of whom he kept as close friends until his death.

In his younger days Dr. Munro was fond of golf, and until the end he was a lover of the country; after tea, from early spring to late autumn, he would drive (always taking friends) to see some interesting place, such as Spye Park in the bluebell season. Every house of note and beauty spot in Somerset and Wiltshire was familiar to him. He died in full harness just as he had wished. S. RANDS

Deaths

WITH deep regret we announce the death of Sir Herbert Jackson on December 10th and of Mr. P. A. Ellis Richards, Past-President of the Society, on December 22nd. Obituary notices will be published later.

Colour Measurement of Opaque Surfaces

BY E. R. BOLTON, F.I.C., M.I.CHEM.E., AND K. A. WILLIAMS, B.SC., F.I.C.

(*Read at the Meeting, November* 4, 1936)

THE success of our efforts in designing a photo-electric instrument for measuring the colours of transparent liquids[1] has prompted us to investigate the possibility of developing a similar instrument for dealing with the colours of opaque surfaces.

We decided at the outset to adopt the spectrophotometric method as the basis for formulating the colour. By this method the amount of light scattered normally from a test surface in various parts of the spectrum is expressed as a percentage of the amount of light similarly scattered from a standard white surface under the same conditions.

The results of measurements at different wave-lengths are plotted in a graph against the wave-lengths, and this leads to a curve describing the colour.

Such a system requires:—(*a*) A source of light illuminating the test colour; (*b*) filters for transforming the light to pure-coloured lights of various narrow wavebands distributed throughout the visible spectrum; (*c*) provision for the removal of ultra-violet and infra-red radiation; (*d*) provision for controlling the intensity of the light; (*e*) a photo-electric measuring system, comprising a photo-electric cell and galvanometer arranged so that the readings of the galvanometer are proportional to the illumination of the photo-electric cell; (*f*) an easily reproducible standard white.

It is also necessary to ensure that the illumination of the surface is such that the light received by the photo-electric cell does not include any glossy reflection from the surface, as this would mask or distort the results.

Luckily this latter requirement proves easy to accomplish if the standard method of illumination used at the National Physical Laboratory is adopted. In this method[2] the test surface is viewed normally and illuminated at an angle of 45°. Surface reflection, due to gloss, leaves the test surface at an oblique angle and does not fall on to the measuring system, and only coloured light scattered in a beam at right angles to the surface is used.

The filters used in the colorimeter for transparent materials were again used for producing light of narrow wave-bands. We have found it possible to supplement these with four more filters to extend the range covered, but for general purposes the original six are quite sufficient, and very little advantage is gained by using the remaining four. Nevertheless, it is interesting to note that these extra filters give points, on all curves in which they have been used, lying satisfactorily in the positions that would be expected.

The density of the filters used rendered it necessary to employ a powerful source of light, and this introduced the problem of disposing of considerable amounts of heat. A 500-watt lamp was used, and the light from this was projected by means of a concave mirror. The accompanying heat is enough to burn or char paper or card several inches away, and we have therefore included a special "condenser" for preventing the bulk of the heat from reaching the test colour. The filters used are also rather sensitive to heat and, to prevent deterioration, we have placed them in the beam reflected from the test surface and not in the illuminating beam. Since reflection of a given coloured light by a surface is independent (for non-fluorescent bodies) of the reflection of accompanying light of other wave-bands, it is immaterial whether the latter are filtered out before or after reflection. Hence measurements with our arrangement will be the same as they would be if the other alternative were adopted.

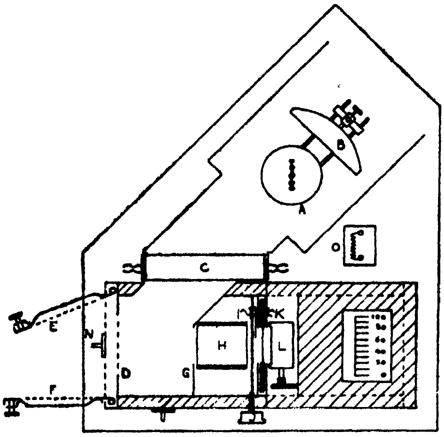

FIG. 1. Plan of instrument.

We found it desirable to include a copper sulphate filter in the instrument to remove all infra-red radiation—even though there is much less of this in a reflected beam than in a direct beam.

Some of the colour-filters, particularly the green ones, transmit a minor band in the red or orange, and this is effectively suppressed by the copper sulphate filter, so that its advantages are twofold.

DESCRIPTION OF INSTRUMENT.—At the back of the instrument (Fig. 1) is the source of light, A, a 500-watt projector lamp connected with the mains. The light from this is concentrated by a concave mirror, B, on to a plate, D, falling thereon at an angle of approximately 45°.

A rectangular glass-sided tank, C, is placed in the beam, and a trickle of cold water is passed through this in order to remove most of the heat from the light-beam and to prevent damage to the test material.

The plate D is provided with a circular opening, and the test surface, F, and a standard white surface, E, held by springs to two pivoted supports, can be swung into exactly the same position behind it. The area of surface exposed to illumination is thus always the same and in the same position. The interior of the instrument is blackened to prevent stray light from affecting the measuring system. Any glossy reflection from the test surface passes off at an oblique angle and falls on to the side of the instrument.

Light scattered approximately normally from the surface at D passes first through a stop at G, then through the filter, H, 2 inches in thickness and filled with a 1 per cent. solution of copper sulphate.

The light then passes a variable shutter, I, controlled by a rotating knob, J. It is filtered by the appropriate colour filters at K; these are mounted on discs in sets of 3 and rotated into position as desired, an indicator outside the instrument showing which is in position.

The light finally falls on the Weston photo-electric cell, L. This is connected with a sensitive calibrated Tinsley galvanometer indicating on a scale at the right-hand side of the instrument. A switch at N controls the main illumination and the galvanometer light, the latter being connected in the main circuit across a shunt, O.

STANDARD WHITE SURFACE.—The standard white surface used in colorimetry is always prepared nowadays by smoking an approximately white surface with burning magnesium. By this means a uniform pure white surface is very easily made, which is readily reproducible and which can be renewed as often as is desired. This method is adopted in our instrument.

COLOUR FILTERS.—The complete set of filters employed is as follows, those marked with an asterisk being additional to normal requirements and not generally used:

Filter		Colour	Head of wave-band transmitted $m\mu$
Wratten,	No. 49	Blue	460
	75	Blue-green	490
	62	Green	530
	73	Yellow-green	570
	72	Orange	610
	71A	Red	640
	*58 45	Bluish-green	510
	*70	Deep red	700
Ilford		*Spectrum yellow	580
		*Spectrum violet	440

MEASURING A COLOUR.—To measure the percentage of light of any given wave-length, scattered normally by a plane test-surface, wheel K is rotated to the appropriate position, the light is switched on, and the standard white surface swung into place behind D.

Shutter I is opened or closed by means of the knob, J, until the galvanometer reads 100. The standard white surface is swung out and the test surface clipped on at F is swung into its place. The galvanometer immediately indicates the percentage required.

By repeating the operation with other filters at K a series of percentages for

I. A. R. I.

light throughout the visible spectrum is obtained, and these figures are plotted on a graph connecting percentages and wave-lengths.

To illustrate the working of the instrument, we have made several measurements of all sorts of colours, and reproduce some typical curves. Figs. 2*a* and 2*b* represent a series of grey painted surfaces, all glossy, and made by mixing black and white paints in various proportions. A black surface, also painted and glossy, was included in the series, and it is gratifying to note that this has given the curve of a true dead-black—namely, a straight horizontal line of zero percentage diffuse reflection. This illustrates how completely the glossy reflection is diverted from the normal beam. The flatness of the curves in Fig. 2*a* is typical of good greys.

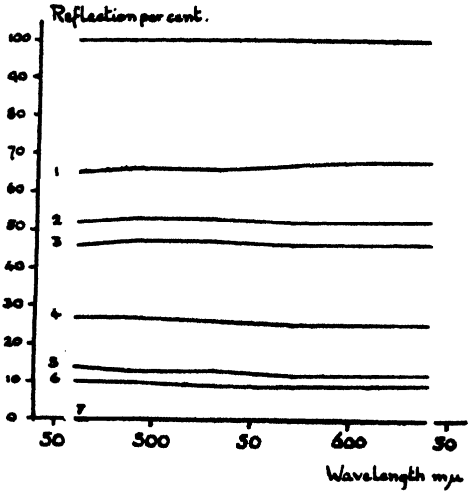

FIG. 2*a*. 1 to 6, greys; 7, black.

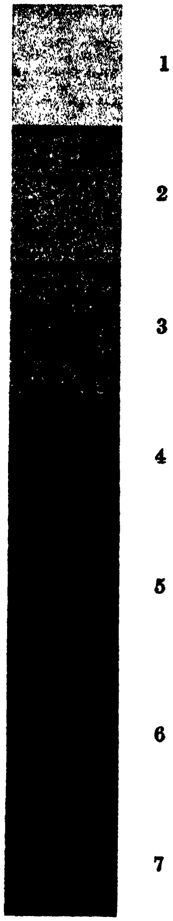

FIG. 2*b*.
1 to 6, greys;
7, black.

Standard white—which by definition gives a horizontal line through the 100 per cent. abscissae—is shown at the top of the series, and the remaining lines represent greys of varying depths. It is very satisfactory to note that the lines are all very nearly horizontal, as should be the case.

We would add that visual photometric examination of these greys indicates that each of them reflects the same percentage of white light as is shown by the graphs.

It may be appropriate to explain at this point that the spectrophotometric definition of white light is a purely conventional one. As mentioned above, it assumes white light to consist of equal quantities of light of all wave-lengths. In actual fact this is, of course, not so, and white light as seen by the eye contains far more yellow and green radiation than either blue or red. International Standard White light is defined as having the energy distribution of a "black body" at a temperature of 5000° K. Its characteristics are known from the work of Ives,[8] and conversion from conventional to actual data may be made, where necessary, by multiplying by the appropriate factor for each wave-length. In general, however, it is simpler to interpret results based on the conventional standard, and we feel that such a method has more general appeal.

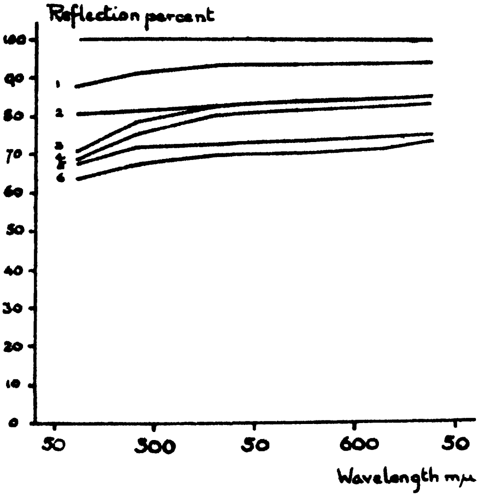

FIG. 3. "White" papers.

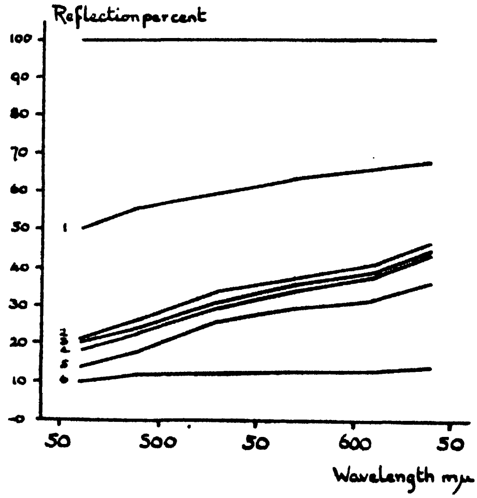

FIG. 4. Brown papers.

Fig. 3 shows the results of examining a number of pieces of "white" paper. Attention is directed to pieces (3) and (4), both of which have a yellowish hue, due to the absorption of blue and reflection of more red and green than blue.

Fig. 4 represents a series of brown papers. Pieces 2, 3 and 4 are so close in colour that they can only just be distinguished by eye. The slightly reddish tinge of piece 5 is clearly shown by relatively higher reflection at the high (red) wavelengths.

Figs. 5, 6, 7 and 8 show reds, oranges, yellows, blues and greens and illustrate the wide application of the instrument.

POWDERS AND PASTES.—The colours so far described have been those of solid opaque surfaces. We have designed a simple cell to slip into the test surface holders, whereby the surface colours of powders and opaque liquids (*e.g.* paints or pasty foodstuffs) may be measured. In such cases, the surface is retained in a vertical position behind a thin sheet of colourless glass. The light non-diffusely reflected from the surfaces of the glass does not increase the actual reading, since it is reflected to the side; but this reflection decreases the amount of light actually falling on to the test surface and reaching the photo-cell. Hence its effect must be compensated. This is readily done by illuminating the standard white surface through a similar colourless glass surface.

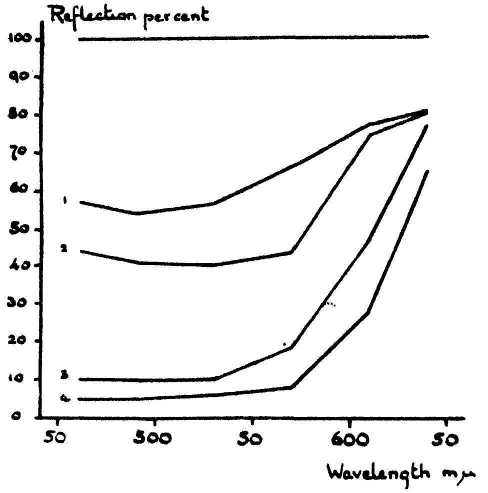

FIG. 5. Red and pink painted surfaces.

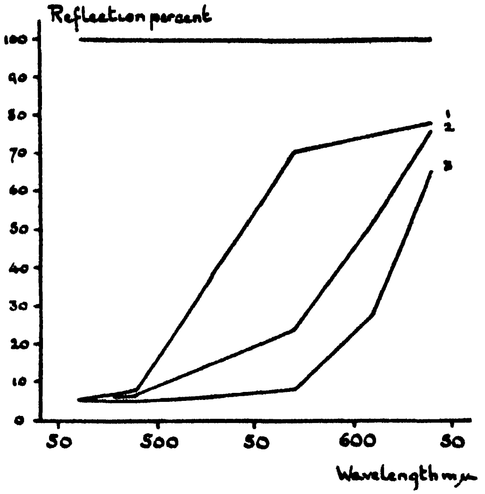

FIG. 6. 1, yellow; 2, orange; 3, red.

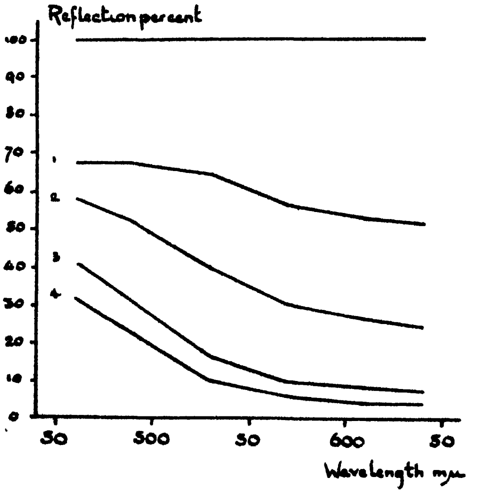

FIG. 7. Blues.

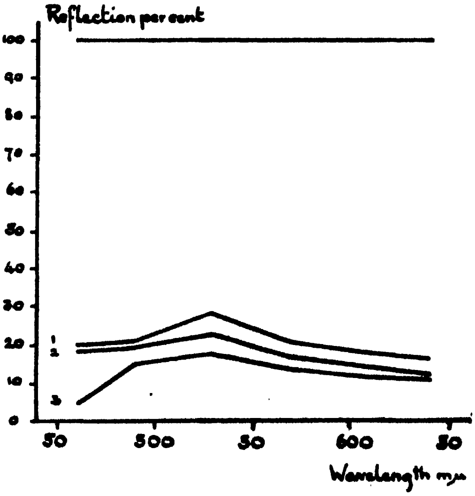

FIG. 8. Greens.

For powders and pastes, therefore, two glass-fronted cell-shaped holders are used—one filled with the test material and the other having the back surface of its glass smoked heavily with magnesium oxide. The cell protects the surface from accidental damage.

This arrangement gives very satisfactory results with powders of all kinds, with liquids such as paints or foodstuffs (*e.g.* mayonnaise creams), and with pastes such as creams, soft fats, or potted meats. In using it, however, it must be realised that many natural colouring matters (notably of meats and peppers) are very sensitive to light, and the reading of the instrument may alter very considerably in a very short time as a result of such exposure. In fact, with colours easily destroyed by bright light, the fading may be observed by the movement of the galvanometer line.

REFERENCES

1. E. R. Bolton and K. A. Williams, ANALYST, 1935, **60**, 447.
2. J. Guild, N.P.L. *Collected Researches*, 1927, **20**, 268, Appendix 2.
3. H. E. Ives, *J. Franklin Inst.*, 1923, **195**, 23.

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LONDON, S.W.3

DISCUSSION

The PRESIDENT, congratulating the authors, said that it was obvious that the apparatus must have innumerable advantages in laboratory and research work; for instance, it would be useful for measuring the degree of fading of colours.

Mr. A. L. BACHARACH, after welcoming the authors' new contribution to colorimetry, hoped that their latest advance would be used in conjunction with the praiseworthy attempt of the British Colour Council to introduce some order into chaos. The ability to express on graph paper the colour of a solid surface at once made it possible to investigate the awkward problem of fading, an especially important matter in connection with standards intended to be permanent. He suggested that the authors should include in the published form of their communication information about the spectral make-up of some of the colours in the Council's Index.

Dr. C. AINSWORTH MITCHELL remarked that the value of this instrument lay in its impersonal application, and it would therefore be useful in criminological work. Thus it could be used to distinguish between different kinds of paper or printing inks of different hue if one had a sufficiently broad band of colour. He asked whether it would be possible to adapt it for measuring the colours of different inks in writing by adapting a horizontal microscope to it.

Mr. A. BLACKIE asked whether it was absolutely certain that the results of the colour analysis would not vary with the particular cell that was used.

Dr. G. MONIER-WILLIAMS suggested that to get a representative curve with some colours it would be necessary to take more than six points as represented by the six screens.

Mr. G. N. GRINLING said that the colour of foodstuffs was often painted over. In that case would the under-colour be picked up and shown on the final graph?

Mr. R. W. SUTTON asked whether the instrument could be applied to fabrics. If so, it would be extraordinarily useful to people who had to deal with the dyeing of textiles; they might be able to get some idea of the fastness to light of colours used.

Mr. H. S. REDGROVE remarked that in the industry with which he was mainly concerned colour was extremely important, and it was necessary to standardise the colours of goods sold. Many firms had installed Lovibond Tintometers for standardising the colours of rouge, face-powder, etc. One advantage of this new apparatus was that it would eliminate the human factor in such cases. Another point was that in the Lovibond Tintometer one represented colours by numerical descriptions; on the surface, this graph method seemed to be more accurate. He asked if the authors had conducted any comparative experiments with the Lovibond Tintometer. There was also the question of packing, for the apparent colour of powders differed according to the packing. Therefore, there would have to be some standard method of pressing powders into the cell. The authors had referred to the fact that certain reds showed a "kick-up" in the blue. They also showed three graphs—two with pure colour and one with a mixture. Had they made any experiments with a view to analysing a mixed colour, knowing what its constituents were? Could they, from a determination of colour, determine the proportions? He mentioned this, because he had made experiments with the Lovibond Tintometer and had obtained a rough analysis but no exact results. If one could do this with this apparatus it was going to be extraordinarily useful. If this instrument were placed on the market, how would it compare in price with the Lovibond Tintometer?

Mr. K. A. WILLIAMS, replying, thanked the meeting for the kind reception accorded to the paper. He said that, while the authors appreciated the classification of the British Colour Committee, they had not adopted its terminology. They preferred instead to describe colours by means of reflection/wave-length graphs. Such a method was, of course, not new, but was in fact one of the earliest suggested. They had not yet had time to relate the colours of the British Index to their instrument, but hoped to do so as soon as they could obtain specimens of suitable size. Repetition of the readings at intervals would give very valuable information about the stability of the colours.

The authors had used a number of Weston photoelectric cells for about 2½ years, and they found the older ones to give the same results as new ones. These cells varied considerably in their actual electric output for a given illumination, but their relative behaviour in different parts of the spectrum appeared to be very consistent. As the figures determined were relative and not absolute, the variations in output were immaterial.

The colour filters used varied in density, but not in line or quality. The authors found that any fading which occurred affected the density but not the quality of the colour. Variation in density did not matter, and both old and new filters gave identical results.

The ten colour filters suggested covered the visible spectrum and were fairly evenly spaced through it. Further points on the graphs could be obtained if and when new filters or combinations of filters became available for intermediate wavelengths. Until then, it was recognised that there must be a possibility of missing, or recording only partially, sharp absorption bands in a colour. Luckily, very few pigments used in commerce on opaque surfaces seemed to show such bands, and the authors had not yet met a case in which their results were vitiated in this manner.

They had not had time to consider the application of their instrument to criminological work. It might be possible to adapt it for use with the microscope, but grave difficulties might be encountered in securing sufficient luminosity of the magnified image.

Referring to a point raised by Dr. Roche Lynch, Mr. Williams described a striking instance of the fading of a bright yellow colour under strong illumination. The fading began almost as soon as the specimen was swung into the light beam, and its progress could be followed by watching the movement of the galvanometer. After a few minutes the fading stopped and the reading became steady.

The effect produced by printing or painting a colour on a surface was almost always affected by the colour of the base, which showed through the superimposed colour to a greater or less extent. This was well known to artists, who used the principle extensively.

The authors had made no attempt to correlate this instrument with the Lovibond Tintometer, though they had established definite relations between the results with their instrument for transparent liquids and the Tintometer.

Mr. Williams said that he had as yet no information about quantitative calculations of the result of admixing two powders. There were obviously several factors involved in such calculations, notably particle size, staining power and the method of packing the powder for observation. He thought that the last of these factors could be standardised without much difficulty.

The Turbidimetric Titration of Gelatin Solutions

By J. F. MORSE

(*Read at the Meeting, November 4th,* 1936)

A REVIEW of the literature[1] concerning the group of degradation products termed gelatin, and its properties, reveals the great complexity of this substance, and it is not surprising, therefore, that conflicting statements as to its physical properties exist.

Gelatin may be prepared by hydrolysis of collagen, contained in the skin, sinews, etc., of animals, or of ossein, the protein of bones. The user of gelatin is chiefly concerned with two of its physical properties, *viz.*, gel strength and clarity. The present communication deals with the latter.

It would appear that the clarity of a gelatin solution is influenced by:—

(1) The ash-content of the gelatin. While in technical practice the nature and amount of ash present in a gelatin may cause turbidity, due to the formation of calcium salts, in laboratory technique turbidity is not usually associated with the ash-content. Arisz[2] and Dhéré and Gorgolewski[3] found that gelatin solutions turbid at a temperature below 30° C. became clear when the temperature was raised above 30° C., this effect increasing with decreasing ash-content. Such turbidity, however, may be due to the colloidal behaviour of the gelatin itself, or it may be connected with change in *p*H value as influenced by the inorganic ions present.

(2) The *p*H of the solution, the maximum turbidity being at the iso-electric point.

Iso-electric values ranging from *p*H 4·0 to 8·0 have been published and serve to show the variable and complex nature of gelatin. Various workers have suggested that gelatin consists of fractions differing in properties. Thus Nagorny[4] obtained two fractions by means of ammonium sulphate, Northrop and Kunitz[5] isolated two fractions by alcohol precipitation at different temperatures, but Sheppard, Hudson and Houck[6] are of the opinion that the "insoluble" fraction is identical with the heat-coagulable proteins derived from the skin, which they isolated in small amounts—less than 1 per cent. Straup[7] flocculated material from a gelatin solution over a temperature range and suggests that the phenomenon is due to fractions. Duclaux and Hirata[8] regard gelatin as existing in two forms, one of which (less than 2 per cent.) scatters white light strongly, with a maximum at *p*H 5.

Provided the pre-treatment of the raw material containing collagen or ossein is carried out in the same way, there appears to be no appreciable difference in the gelatin obtained from the two types of material. Acid and alkali pre-treatment, however, certainly produce gelatins of differing properties, and Briefer[9] has shown that the difference is so characteristic as to be uninfluenced by subsequent removal of mineral matter.

Kraemer and Dexter,[10] Briefer[9] and Sheppard and Houck[11] have shown that gelatins from acid-treated raw material have a maximum zone of turbidity in the region of *p*H 7 to 8, whilst lime-treated stock gave values in the neighbourhood of *p*H 4·7 to 5·0. Sheppard and Houck, however, found their material to give maximum alcohol precipitation at *p*H 4·9, indicating that the substance, or substances, giving turbidity at *p*H 7 to 8 did not constitute the major portion of the sample.

The fact that acid-treated raw material yields a gelatin differing in properties from that obtained from lime-treated stock, and that subsequent purification does not alter the properties conferred by these treatments may, in part, account for the different results recorded by various workers using gelatins from raw material whose origin and pre-treatment were unknown, however thorough the laboratory purification may have been.

Regarding turbidity simply as a physico-chemical property and not necessarily as an indication of iso-electric point, agreement exists that for acid-treated raw material it is at a maximum in the neighbourhood of *p*H 8 and that lime-treated stock yields a gelatin with a maximum turbidity about *p*H 5.

Various methods for comparing the turbidities of gelatin solutions have been employed, *e.g.* visual inspection, intensity of scattered light at right angles to the Tyndall beam, a photo-electric cell being used, and nephelometric determinations.

Such measurements require the preparation of a number of samples of differing *p*H values and strictly comparable thermal histories. Moreover, the preparation of a sufficiently large number of samples accurately to cover the *p*H range 3 to 9 is a laborious task. The method here described is rapid, and the *p*H of maximum turbidity of a gelatin, as determined by it, is unaltered by the differences in technique so far explored.

Fig. 1 shows the apparatus employed to determine the "turbidity" curve of gelatin (and other proteins). Fittings from a Leitz Large "Uma" Photomicrographic apparatus formed the basis of the arrangement. The optical bench was the auxiliary fitting supplied on which to clamp accessory apparatus. The source of illumination, A, was a 6-volt 5-amp. projection lamp run from a 10-volt car accumulator. Under these conditions 6 amps. were passed through the lamp, and absolutely steady illumination was obtained during the course of a titration. Fluctuations in current of the mains supply rendered it impossible to run the lamp by means of resistances. The aspherical focussing condenser, B, and iris diaphragm, C, served to obtain the optimum condition of the light beam. Behind the condenser a filter-carrier and its accessories were constructed and fitted (D). The carrier received two glass strips containing Wratten filters in the form of gelatin films 1-inch square. A clicking arrangement allowed the filters to be adjusted easily and correctly.

The titration was carried out in the glass cell, E, having parallel sides and a curved bottom. The capacity was 450 ml. and the stratum 6 cm.

The light beam, after leaving the cell, was received by the Weston Photronic photo-electric cell, F. A "Z" type glass stirrer, G, gave rapid and effective mixing without aeration or undue surface agitation. Additions of acid and alkali were made by means of the burette H.

Measurement of pH was by means of an antimony electrode in conjunction with a saturated KCl calomel cell, such an arrangement having proved most satisfactory in these laboratories over a period of eight years. Other electrode systems could, of course, be used. A Cambridge slide-wire potentiometer, together with a Weston normal cell and a 2-volt accumulator, were used for the determinations. A Cambridge micro-ammeter reading to 6 micro-amperes was employed as a null-point galvanometer, and after the pH value had been determined this meter was switched over to the photo-electric cell and the current output read directly to 0·05, and by estimation to 0·01 micro-ampere.

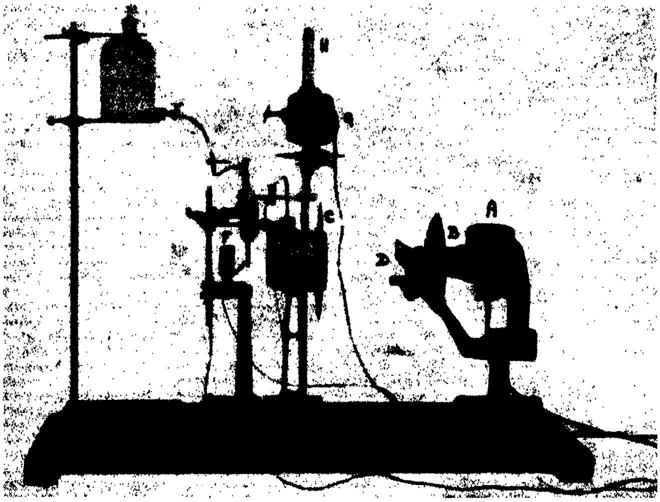

Fig. 1.

The stirrer, calomel and antimony electrodes and burette were so arranged that no interruption was offered to the beam of light, and screens (not shown in Fig. 1) were fitted so that no extraneous light reached the photo-electric cell.

The method adopted was as follows:—Six g. of gelatin were soaked in 100 ml. of distilled water until thoroughly hydrated, and the mixture was then warmed to about 40° C., care being taken to avoid local over-heating. When solution had been effected, 200 ml. of cold water were added, giving 300 ml. of 2 per cent. gelatin solution. The light, with the selected filter, was adjusted to give a convenient deflection of the meter, and the highest reading recorded during an estimation was regarded as representing no light scattered.

The following factors which might influence the results were then investigated:—(*a*) Wave-length of light employed; (*b*) temperature of the solution; (*c*) type of acid employed for adjustment; (*d*) "direction" of titration.

(*a*) WAVE-LENGTH OF LIGHT EMPLOYED.—The following Wratten filters were used:—49 (C4), 75, 62, 73, 72, 70. The predominant wave-lengths transmitted (as stated by the makers) were 460$m\mu$, 490$m\mu$, 530$m\mu$, 570$m\mu$, 610$m\mu$, and 700$m\mu$, respectively. An Ilford infra-red filter, transmitting at about 800$m\mu$, was also employed. Filters transmitting infra-red light (apart from the Ilford filter), *viz.* 73, 72 and 70, were used in conjunction with an aqueous copper sulphate filter inserted between the filter and containing cell (*cf.* Bolton and Williams, ANALYST, 1935, 60, 449).

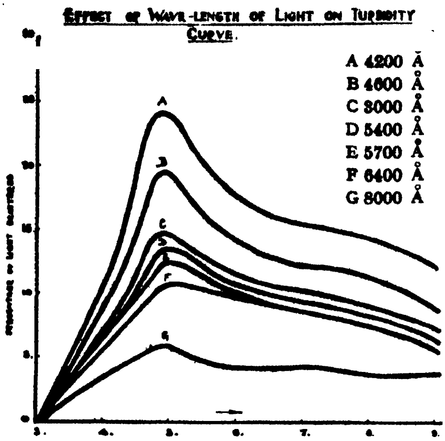

FIG. 2.

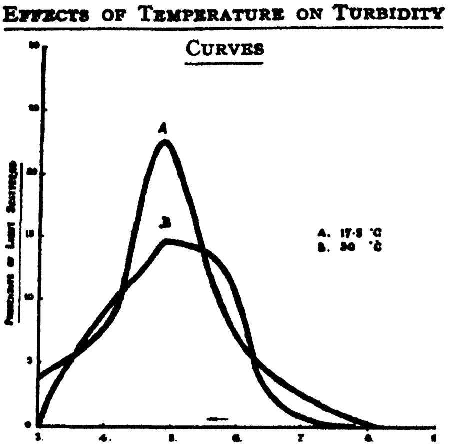

FIG. 3.

For these and the following experiments a high-grade commercial powdered gelatin was used. Fig. 2 illustrates the results, titration being from pH 3 to 9. It will be noted that the light scattered increases as the wave-length decreases, the difference between the infra-red and blue light being very noticeable. This increased scattering with short wave-lengths was to be expected, and Rawling[12] has published photographs of the phenomenon. It will be seen that the pH of maximum turbidity is independent of the wave-length of light employed. The Wratten No. 49 (C4) blue filter was selected for subsequent work, as the most accurate results were to be expected with light of short wave-length.

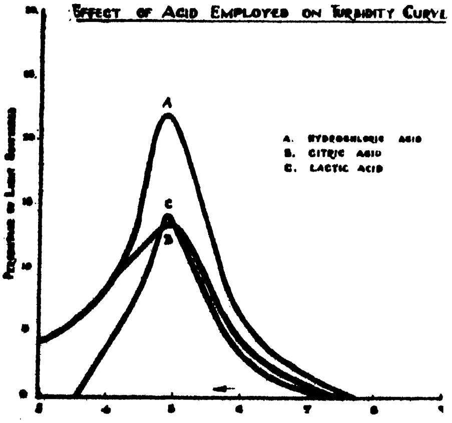

FIG. 4.

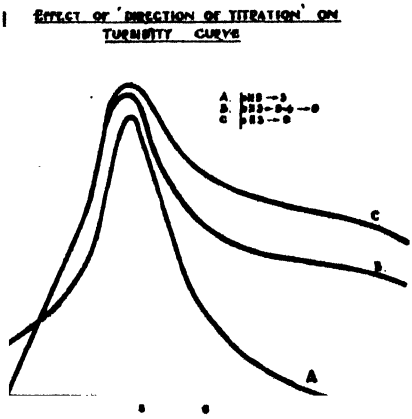

FIG. 5.

(*b*) THE EFFECT OF TEMPERATURE.—Kraemer and Dexter[13] investigated the effect of temperature on gelatin solutions. Fig. 3 shows the effect on the "turbidity curve." Although the general contour is somewhat modified, the point of maximum turbidity is unchanged.

(*c*) THE TYPE OF ACID EMPLOYED.—In all work hydrochloric acid and caustic soda were employed to adjust the reaction. Fig. 4 shows the effects of hydrochloric, citric, and lactic acids, the last two being tried because they are frequently employed with gelatin in various food products.

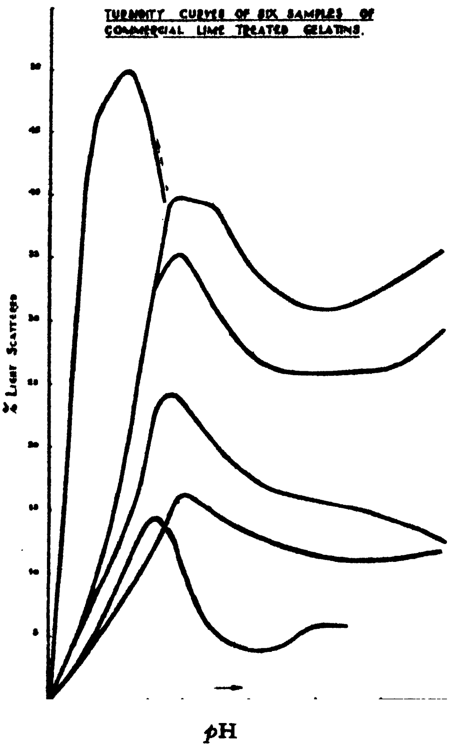

FIG. 6.

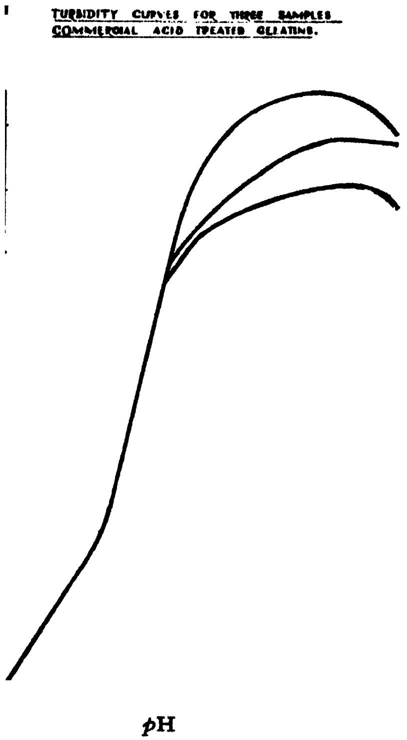

FIG. 7.

(*d*) THE DIRECTION OF TITRATION.—Fig. 5 compares the results obtained by the three methods available, *i.e.* from *p*H 3 to 9, from *p*H 9 to 3, and from the *p*H of the freshly prepared gelatin solution in each direction.

From the foregoing results it will be seen that in every instance the *p*H of maximum turbidity is the same. Minor differences in the form of the curves exist, particularly noticeable being the sharp maximum turbidity when the direction of titration is *p*H 9 to 3.

If maximum accuracy be desired, the titration should be carried out with hydrochloric acid from *p*H 9 to 3, with the use of blue light and at a low temperature (but not low enough to cause gelling of the solution). Very dark solutions may necessitate the use of a yellow or orange filter. As far as possible, conditions similar to those to be encountered by the gelatin should be arranged, and whatever method be employed, the point of maxim tumurbidity should be the same.

EXAMINATION OF COMMERCIAL GELATINS.—A series of commercial gelatins was examined by the technique outlined above. Gelatins from lime-treated stock gave points of maximum turbidity ranging from pH 4·2 to 5·1. Good-grade gelatins were usually at their maximum turbidity in the neighbourhood of 4·9, and there appeared to be little connection between the grade of gelatin and the amount of light scattered. Fig. 6 shows the curves obtained with commercial gelatins of varying grades. A Scotch glue solution, 0·1 per cent. concentration, had maximum turbidity at pH 4·65 and scattered 95 per cent. of the original incident light.

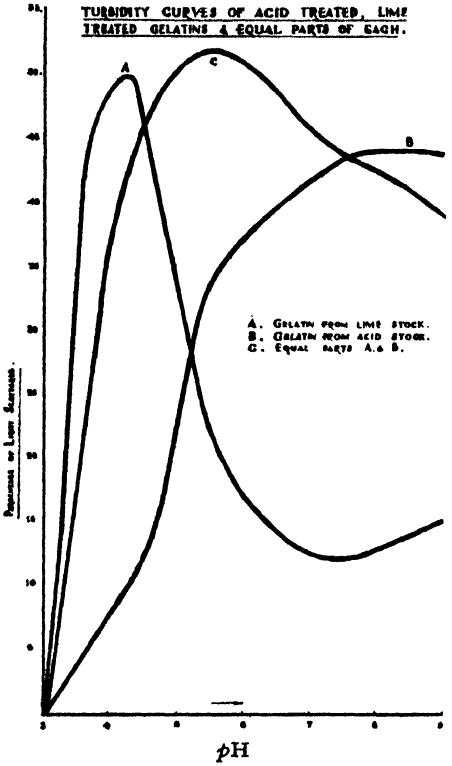

FIG. 8.

Three samples of gelatin from acid-treated stock gave the curves illustrated in Fig. 7. As noted by other workers,[9,10,11] a sharp maximum was not obtained, but a zone between pH 7 to 9 with a maximum at pH 8. A sample of each type of gelatin was dissolved in water and the turbidity curve of the mixture was obtained. Fig. 8 shows the curves of the two gelatins and of the mixture. It will be noted that two turbidity maxima are not apparent, but a new one, between those of the two gelatins, occurs. This phenomenon has been observed by Kraemer,[14] and is receiving detailed investigation in this laboratory.

Preliminary work with proteins other than gelatin, *viz.* peptone, white-of-egg, and isinglass, indicates that the method has wide application.

SUMMARY.—(1) A method for the rapid determination of the "turbidity" curve of a gelatin solution over the pH range 3 to 9 has been described.

(2) With commercial gelatins, prepared from lime- and acid-treated stocks, the generally accepted pH 4·9 and pH 7 to 8 as regions of maximum turbidity, respectively, were obtained. Two distinct maxima were not obtained with mixtures of the two types of gelatin.

(3) The application of the method to other water-soluble proteins has been indicated.

In conclusion, grateful acknowledgment is made to Dr. William Clayton for suggesting this method and for his advice and criticism during the investigation.

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RESEARCH LABORATORY
36, CRIMSCOTT STREET
BERMONDSEY, LONDON, S.E.1

DISCUSSION

Mr. D. M. FREELAND asked the author what point of the maximum turbidity was, in his opinion, the iso-electric point. A great deal of work had been published by the Adhesives Research Committee of the Department of Scientific and Industrial Research (1922, 1926, 1932), who endeavoured to prepare a very pure gelatin by dialysis and other means. They found an iso-electric point of *p*H 4·7. He wondered whether, in this connection, the author had dialysed any gelatin, and whether the mineral matter present affected the turbidity to any large extent.

Mr. J. F. MORSE replied that, in his experience, the *p*H of maximum turbidity depended on the degree of hydrolysis and in laboratory experiments values from *p*H 4·2 to 5·2 had been obtained. A value of *p*H 5·7 seemed intermediate between the products of acid and alkali hydrolysis. Maximum turbidity at *p*H 8 to 9 did not necessarily indicate the iso-electric point, although it might possibly be that of a fraction of the sample. He had not dialysed gelatin, but the literature was full of such processes, and the different iso-electric points found for the purified material were doubtless due to the various gelatins used.

Dr. W. CLAYTON said that this work was commenced after the reading of various papers which included findings for the iso-electric point of gelatin ranging from *p*H 4 to *p*H 8, and the opinion, moreover, that gelatin possessed two iso-electric points. Such contradictory data warranted fuller inquiry. Within the last eighteen months there had appeared a number of papers, particularly from Russia, which seemed to point to the presence in gelatin of at least five fractions, characterised, so far, simply as different micelles of gelatin. The relation of maximum turbidity and the iso-electric point was an important matter for investigation, especially concerning their coincidence or not. He concluded by saying that gelatin was the most nondescript material that the food chemist was called upon to examine from a physico-chemical standpoint.

Dr. E. B. HUGHES remarked that he was very interested in this paper. The difference that had been shown between lime-treated gelatin and acid-treated gelatin in respect of clarity would be of importance in the use of gelatin in foods where clarity was required. He fully agreed that commercial gelatin was a heterogeneous material and that there were always degradation products present to some extent, a small amount of such appreciably reducing the gold number of the gelatin, which was not, however, further reduced by larger amounts of the degradation products. Rendering the gelatin "ash-free" did not affect the gold number, but did greatly affect solubility and the character of the gel. He found the results and conclusions reported in this paper to be particularly interesting in that they were in accordance with Loeb's theory, of which he also was a supporter.

Mr. T. MCLACHLAN pointed out that the material employed in the manufacture of gelatin was not a pure product and that treatment with acid or alkali gave hydrolysis products. According to the type of hydrolysis used so one obtained different end-products.

Professor HUGGETT said that he was extremely interested in the physiological aspect of this paper. Most of the speakers had emphasised the significance of the origin of the gelatin. It was essentially a heterogeneous product, the properties of which depended on its original source. For all practical purposes it contained, from a nutritional point of view, little or nothing of importance. It contained none of the essential acids and no vitamins and was characterised as "a second-rate protein." Its physico-chemical properties were variable in the sense that they depended upon the fact that the gelatin was extracted from different types of animal material.

Dr. J. H. HAMENCE asked what type of curve was obtained when the gelatin solution had in it a small amount of insoluble mineral matter in suspension, and whether such an impurity had any influence on the maximum value given by that particular gelatin.

Mr. MORSE replied that, so far as he could see, it would have no effect whatever.

A Scheme for the Separation and the Determination of Metallic Impurities in Foodstuffs

BY J. HUBERT HAMENCE, M.SC., PH.D., F.I.C.

WITH the increasing attention now given to the presence of traces of metallic impurities, such as tin and lead, etc., in foodstuffs, it was thought desirable to produce a scheme whereby all the heavy metals which commonly occur as impurities might be determined in the same solution.

The general tendency to-day is to test separate portions of the sample, each for a different impurity. This procedure is a perfectly good one when the substance is readily obtained in solution and a colorimetric test can be applied directly to that solution without any previous separations. In the majority of instances, however, this is not the case, and when complex organic bodies, such as foodstuffs, are being dealt with, the conversion of three or four portions of the same sample into a condition suitable for applying the colorimetric tests involves much time and labour.

Many of the tests for traces of heavy metals necessitate the absence of interfering bodies, so that in these instances some form of separation becomes necessary before the final test can be applied.

ANALYTICAL DETAILS

PREPARATION OF THE SOLUTION AND SEPARATION STAGE I.—In dealing with organic compounds 20 g. are destroyed by the wet oxidation process, and the final colourless sulphuric acid solution is diluted with 50 ml. of water and evaporated once more to the fuming stage, or, if a portion of this solution is to be employed for the determination of arsenic, 25 ml. of saturated ammonium oxalate solution are added instead of the water.

The sulphuric acid solution is again diluted with water, and the contents of the Kjeldahl flask are filtered into a beaker, any insoluble matter left on the filter being washed back into the flask, and boiled with conc. hydrochloric acid. After dilution, this solution is also filtered into the beaker, and the flask is finally rinsed out with distilled water. In the resulting solution (which should now amount to about 50 ml.) is dissolved 2 g. of citric acid of analytical quality and 10 mg. of crystalline ferrous sulphate.

If, however, ashing be preferred to wet oxidation, 20 g. of the sample are incinerated at a low temperature, in a silica basin. To the ash 5 ml. of conc. hydrochloric acid are added, and the liquid is evaporated to dryness on a water-bath. The residue is dissolved in a mixture of 5 ml. of conc. hydrochloric acid and 20 ml. of water and the solution is filtered. The citric acid and ferrous sulphate are added to this solution.

The solution, thus obtained, is cooled, and, after the addition of three drops of universal indicator solution, is treated with ammonia until a green colour is obtained, indicating a *p*H of about 8, the solution being cooled during this addition.

Hydrogen sulphide is then passed through the solution for 20 minutes, and the precipitate is filtered off on a small No. 2 Whatman paper. The precipitate is washed well with dilute ammonium sulphide solution. This solution is prepared by adding ammonia (sp.gr. 0·880) to water saturated with hydrogen sulphide until the liquid smells distinctly of ammonia. It is important that the precipitate should be washed free from ammonium citrate.

Tin.—The tin can now be determined in the filtrate. One method of achieving this, and the one that has been employed to obtain the results given at the end of this paper, is to render the filtrate acid with hydrochloric acid after the addition of 2 ml. of yellow ammonium sulphide solution, when the tin will be precipitated with the sulphur. After standing for some time the precipitate is filtered off, washed with hydrogen sulphide water and burnt to tin oxide.

Alternatively, the filtrate and washings may be made up to 100 ml. and the tin in an aliquot part determined by Clark's 4-methyl-1.2-dimercaptobenzene reagent[1] in the following manner:

To 10 ml. of the solution are added 2 drops of thioglycollic acid, the solution is neutralised to litmus, and 10 drops excess of conc. hydrochloric acid, followed by 0·5 ml. of reagent,[1] are added.

The red colour developed on warming is matched against standards containing known amounts of tin and the same quantities of reagents.

SEPARATION STAGE II.—The black sulphide precipitate is dissolved by gently warming the filter-paper, containing the precipitate, in a mixture of 20 ml. of water and 2 ml. of conc. nitric acid. When the sulphides have completely dissolved the filter-paper is picked out with a glass rod and replaced in the funnel. The solution is filtered through the same filter, which is subsequently washed with hot water. The filtrate and washing should amount to about 50 ml.

To the filtrate is added 1 g. of ammonium sulphate of analytical quality, and the solution is heated until near the boiling-point; the iron is precipitated by the addition of 15 ml. of 15 per cent. w/v ammonia solution, and the heating is continued until the ferric hydroxide has coagulated. It is important that the solution should not be boiled for long during this precipitation, because if most of the ammonia is boiled off, material adsorption of the copper may result.[2] The precipitate is filtered off, and washed with hot water and 2 per cent. ammonia solution, and the filtrate is reserved for the determination of zinc and copper.

SEPARATION STAGE III.—The ammonia precipitate from the Separation Stage II is dissolved by warming the filter-paper and precipitate with a mixture of 2 ml. of conc. nitric acid and 20 ml. of water; the solution is filtered through the original filter and the filter is washed with hot water. The filtrate is made up to 50 ml.

Bismuth.—To 15 ml. of the filtrate are added 5 ml. of saturated ammonium thiocyanate solution and 5 ml. of water, and the solution is extracted with successive quantities of 10 ml. of ether until the last ethereal wash is colourless; four washes are usually necessary. To the aqueous solution 5 ml. of the ammonium thiocyanate reagent are then added (for preparation of the reagent see end of paper). A yellow colour indicates the presence of bismuth. The bismuth, if present, may be determined by matching the yellow colour against standards prepared by adding known amounts of bismuth nitrate solution to 15 ml. of water and 15 ml. of reagent, and extracting the mixture once with 10 ml. of ether.

Lead.—If no bismuth is found, the lead is determined in 25 ml. of the filtrate, after removing the iron by adding 5 ml. of saturated ammonium thiocyanate and extracting the ferric thiocyanate with a mixture of amyl alcohol and ether.[3]

If bismuth is present, the lead is determined after the iron and bismuth have been extracted by the pyridine thiocyanate process.[4] (See also the paper by Roche Lynch and his co-workers.[5])

SEPARATION STAGE IV.—*Copper.*—The filtrate from the ammonia precipitation of Separation Stage II is made up to 100 ml., and the copper in a portion of it is determined by means of the diethyl dithiocarbamate reagent.[6]

Zinc.—If copper is present, it must be removed before testing for zinc; this is achieved as follows:—The remainder of the solution is evaporated to 20 ml. and then warmed with 5 ml. of 4 *N* hydrochloric acid to dissolve any traces of zinc that have become adsorbed by the glass during the evaporation. The solution is cooled, 1 mg. of copper (as copper sulphate) is added, and the whole of the copper is precipitated with hydrogen sulphide. The addition of copper enables traces of copper to be removed more effectively. The precipitated cupric sulphide is filtered off, the precipitate is washed with hydrogen sulphide water, and the filtrate is evaporated to 20 ml. The zinc is determined with 8-hydroxyquinoline in the following manner:—To the concentrated filtrate are added 5 ml. of 20 per cent. ammonium acetate solution, and the *p*H of the solution is adjusted to about 7·5 by the addition of ammonia, two drops of universal indicator being added for this purpose. Two ml. of a 2 per cent. solution of 8-hydroxyquinoline in *N* acetic acid are then added, and the solution is boiled for 5 minutes in a covered beaker. The "oxine" precipitate, which is obtained in a crystalline form, is filtered off after standing for several minutes and washed with hot water. The filter is then washed twice with 3 *N* hydrochloric acid and twice with water, the washings, which should amount to 30 ml., being collected in a stoppered bottle. To this, *N*/50 bromide and bromate solution (see end of paper) is added until a drop of the solution yields a blue reaction when tested with starch iodide paper, 2 ml. excess being then added and the solution well shaken. After standing for several minutes in the dark potassium iodide solution is added, and the excess of bromine is determined by titration with $N/50$ thiosulphate solution. One ml. of bromine solution absorbed ≡ 0·163 mg. of zinc.

The scheme just described, by which tin, lead, bismuth, copper and zinc may be determined quantitatively, all in the same solution, is summarised below.

GENERAL SCHEME OF THE SEPARATIONS

1. Hydrogen sulphide is passed into the solution, to which a trace of ferrous sulphate has been added and the pH is adjusted to 8; the precipitate is washed with dilute ammonium sulphide solution.

Filtrate

TIN is determined in this solution either by precipitation as sulphide, effected by addition of ammonium sulphide followed by excess of hydrochloric acid; or colorimetrically by 4-methyl-1.2-dimercaptobenzene reagent.

2. *Precipitate*

This is dissolved in dilute nitric acid and the iron precipitated by an excess of ammonia in the presence of ammonium sulphate. The precipitate is washed with ammonia and hot water.

3. *Precipitate*

This precipitate will contain the hydroxides of lead and bismuth adsorbed on the ferric hydroxide. BISMUTH is tested for and determined as the yellow thiocyanate, and LEAD is determined after the removal of the iron, and bismuth, if any, by the thiocyanate process.

4. *Filtrate*

COPPER is determined directly with diethyl dithiocarbamate in a portion of the filtrate.

ZINC is determined in the remainder by 8-hydroxyquinoline after the removal of the copper, if any, by hydrogen sulphide precipitation in the acid solution.

Part of this scheme—namely, that part embodying the separation of lead, copper and zinc—has been adopted by the "Investigatory Panel on Methods of testing Gelatin" of the British Standards Institution, for the determination of heavy metals in gelatin.

Bismuth, although not a common impurity in foodstuffs, has been included in this scheme owing to its significance in toxicological work in which it is sometimes necessary to determine traces of bismuth and also to determine traces of lead, etc., in the presence of bismuth.

EXPERIMENTAL SEPARATIONS.—The efficacy of the scheme was tested in the following manner:—A solution containing 0·10 g. of calcium carbonate, 0·10 g. of sodium phosphate and 5 ml. of conc. sulphuric acid in 50 ml. of water was prepared to simulate in some respects the solution that is obtained after the destruction of an organic material by wet oxidation. To this solution were added known amounts of the various metals, and the resulting mixtures were subjected to the separations described in this paper.

Expt.		Tin mg.	Lead mg.	Bismuth mg.	Copper mg.	Zinc mg.
A.	Added	5·0	0·04	—	0·06	—
	Found	4·8	0·04	—	0·07	—
B.	Added	0·0	0·50	0·0	0·25	1·00
	Found	0·0	0·48	0·0	0·25	0·95
C.	Added	—	0·15	0·50	0·15	—
	Found	—	0·13	0·47	0·16	—
D.	Added	—	—	—	—	0·22
	Found	—	—	—	—	0·23
E.	Added	30·0	0·25	1·0	0·05	0·20
	Found	30·4	0·24	*	0·06	0·08†
F.	Added	1·0	0·20	0·0	0·22	0·30
	Found	1·2	0·20	0·0	0·24	0·26

* Bismuth detected but not determined. † See p. 23.

Other experiments have been made with a variety of foodstuffs and organic materials, and the results of the determination of heavy metals obtained by these separations have been checked by other methods, which have been in use for some years, with satisfactory agreements. It is important that blank experiments should be made on each new batch of reagents.

DISCUSSION.—*Tin.*—Only a limited number of experiments have been made with Clark's 4-methyl-1.2-dimercaptobenzene reagent, but these indicate that the reagent is best employed when the quantity of tin is of the order of 50 parts per million or less. These experiments appear to indicate that the standards should be prepared from water saturated with hydrogen sulphide and should contain the same amounts of ammonium sulphate and ammonium citrate as are in the solution that is being tested. The concentration of hydrochloric acid is also important in the reaction, since a large excess of hydrochloric acid inhibits the production of the red coloration.

Also by the preliminary separation of the tin, as described in Separation Stage I, the interference produced by other metals which yield coloured mercaptides, notably bismuth giving a brick red mercaptide, is avoided.

Bismuth.—The method described for the detection and determination of traces of bismuth is a modification of that first described by Heinrichs and Hertrich.[7] These workers made no attempt to avoid interference due to traces of iron in the reagents. In the procedure here described iron is extracted as the thiocyanate with ether, and copper, the only other metal besides bismuth which yields a yellow thiocyanate, is removed during the ammonia precipitation prior to the test. This colour test for bismuth can be applied only after the metal has been separated from large amounts of mineral salts in the manner indicated, because the presence of these would destroy the yellow colour. Traces of lead do not interfere with this method of determining bismuth, and by it 0·02 mg. of bismuth may be detected.

The thiocyanate reagent is prepared by adding 25 ml. of saturated ammonium thiocyanate solution to a mixture of 10 ml. of water and 1·5 ml. of conc. nitric acid and diluting the whole to 50 ml. This solution is extracted with 10 ml. of ether and 10 ml. of amyl alcohol, which removes any iron that may be present.

Zinc.—The use of yellow ammonium sulphide for washing the hydrogen sulphide precipitate in Separation Stage I is to be avoided. Low results for the zinc have been obtained when this procedure is adopted, as is shown by experiment E.

But the use of dilute yellow ammonium sulphide for this washing may become necessary when large quantities of tin (400 p.p.m. and over) are present. This procedure has no effect on the determination of the lead, bismuth or copper, but it may produce low results for zinc.

The $N/50$ bromide and bromate solution is prepared by dissolving 0·554 g. of potassium bromate and 2·24 g. of potassium bromide in 1 litre of water, and is standardised against $N/50$ thiosulphate.

Should the filter-paper become "pulped" during the boiling with dilute nitric acid in Separation Stages II and III the solution, together with the pulp, must be filtered through a new "well washed" filter-paper.

I wish to thank Dr. Bernard Dyer and Mr. George Taylor for their interest in this work.

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DR. DYER'S LABORATORY
17, GREAT TOWER STREET
LONDON, E.C.3

A Rapid Method for the Determination of Antimony in Lead-Rich Alloys

BY K. STANFORD, B.SC., AND D. C. M. ADAMSON, A.I.C.

THE determination of antimony in lead-rich alloys by Low's original method[1] (digestion in concentrated sulphuric acid followed by titration with potassium permanganate in the presence of hydrochloric acid) may be vitiated by the fact that antimony is adsorbed by lead sulphate, which is precipitated on dilution of the digest. This phenomenon has been noted by a number of workers,[6,4] and their attempts to remedy it, although differing in detail, are similar in principle. Some add hydrochloric acid to the solution and boil, the amount added varying with different observers,[2,3] whilst others prefer to filter off the lead sulphate, dissolve it in hydrochloric acid, and titrate the solution either separately or after adding it to the filtrate from the lead sulphate.[4,7]

In any event, hydrochloric acid is required for the rapid oxidation of tervalent to quinquevalent antimony by potassium permanganate (the method of Demorest[5] and McCabe[6] of adding permanganate in excess and back-titrating with ferrous ammonium sulphate in the absence of hydrochloric acid has received some criticism), and Pugh[7] has stated that the addition is necessary if the reaction—

$$4MnO'_4 + 5Sb_2O_3 + 12H^{\cdot} = 4Mn^{\cdot\cdot} + 5Sb_2O_5 + 6H_2O$$

is to proceed stoichiometrically under normal conditions, and has also shown that certain relative concentrations of hydrochloric and sulphuric acids should be maintained.

To dissolve the alloy in sulphuric acid, a long digestion is necessary, the time required varying with the particle size of the alloy, and Evans[8] considers this to favour adsorption. To overcome the difficulty of solution of the alloy with its attendant dangers of adsorption, it was decided to fuse the alloy, intimately mixed with potassium bisulphate. In every instance the reaction between the alloy and the bisulphate was complete in three to four minutes, giving a homogeneous melt which could be readily extracted with dilute hydrochloric and sulphuric acids. The resulting solution was titrated, cold, with standard permanganate solution.

In order to establish the accuracy of the method, the scheme adopted in this investigation was to make a number of determinations, using the following substances:—(i) pure antimony alone; (ii) pure antimony plus lead; (iii) lead-antimony alloys; (iv) lead-antimony alloys containing arsenic and tin. The same method was used for all the determinations as follows:

METHOD.—An accurately weighed amount of substance (1 g. of alloys) is intimately mixed with 5 g. of potassium bisulphate in a porcelain crucible, 2 in. in diameter, and gently heated. The reaction is fairly vigorous and spattering may occur in the early stages, but it was found that, with care, it was unnecessary to cover the crucible with a lid. The temperature is then raised to give a homogeneous melt, which with antimony alone is clear, but with alloys is white and opaque; it is unnecessary to proceed beyond this stage, and it was observed that the particle size of the alloy has little effect on its speed of disintegration.

TABLE I

ANTIMONY ALONE

Antimony taken g.	$KMnO_4$ used (1 ml. = 0·0061 g. Sb) ml.	Antimony found g.	Error g.
0·0500	8·20	0·0502	+0·0002
0·0967	15·80	0·0964	−0·0003
0·1000	16·36	0·0998	−0·0002
0·1114	18·20	0·1110	−0·0004
0·1500	24·60	0·1501	+0·0001
0·2034	33·28	0·2030	−0·0004

While the crucible is cooling, a mixture of 10 ml. of conc. hydrochloric acid, 30 ml. of conc. sulphuric acid and 200 ml. of water is prepared in a 400-ml. beaker, and the crucible and contents are placed in this. When the melt is detached, the crucible is removed and rinsed, and the solution is boiled for a few minutes, then cooled to 5 to 10° C., and titrated with potassium permanganate solution which has been standardised with sodium oxalate. The end-points are apparent for half-a-minute, but this period can be increased to three or four minutes if the bulk of the solution titrated be increased to 350 ml. Alternatively, the solution may be titrated at about 60° C. with potassium permanganate solution, a few drops of 0·05 per cent. methyl orange solution being added as an indicator.

Table I gives the results obtained with pure antimony; Table II those with pure antimony plus 1 g. of pure lead.

TABLE II

ANTIMONY PLUS 1 G. OF LEAD

Antimony taken g.	$KMnO_4$ used (1 ml. = 0·0061 g. Sb) ml.	Antimony found g.	Error g.
0·0397	6·48	0·0395	−0·0002
0·0601	9·90	0·0604	+0·0003
0·1000	16·45	0·1004	+0·0004
0·1507	24·78	0·1512	+0·0005

It appears, therefore, that the reaction is quantitative, and that in the presence of lead no adsorption is detectable.

DETERMINATION OF ANTIMONY IN LEAD-ANTIMONY ALLOYS.—Three alloys containing approximately 2·0, 4·5 and 10 per cent. of antimony, respectively, were prepared by melting together the requisite proportions of antimony and lead. The alloys were chill-cast and their outer layers removed by filing. The samples for analysis were prepared by removing about 100 g. from each alloy with a rasp; these portions were washed with ether to remove grease, and extraneous iron was removed with a magnet. Full analyses of the alloys were made independently by us, the antimony being determined gravimetrically as Sb_2O_4 and volumetrically by the Györy method, with the following results:

TABLE III

	ALLOY 1 Per Cent.	ALLOY 2 Per Cent.	ALLOY 3 Per Cent.
Lead	97·89	95·40	89·88
Copper	0·07	0·05	0·08
Iron	0·04	0·04	0·07
Arsenic	Nil	Nil	Nil
Antimony (by diff.) ..	2·00	4·51	9·97
—— (gravimetrically) ..	2·03	4·56	9·88
	2·05	4·59	10·09
—— (Györy's)	2·03	4·46	9·95
	2·05	4·51	9·95
(Average) ..	2·04	4·53	9·97

Table IV shows the results obtained by the proposed method, for the antimony-content of these alloys (1 g. was taken in each case).

TABLE IV

ALLOY 1

Antimony (diff.) Per Cent.	$KMnO_4$ (1 ml. = 0·00203 g. Sb) ml.	Antimony found Per Cent.	Error Per Cent.
2·00	9·80	1·99	−0·01
	9·92	2·01	+0·01
	9·82	1·99	−0·01
	9·90	2·01	+0·01

ALLOY 2

Antimony (diff.) Per Cent.	$KMnO_4$ (1 ml. = 0·0061 g. Sb) ml.	Antimony found Per Cent.	Error Per Cent.
4·51	7·36	4·49	−0·02
	7·48	4·56	+0·05
	7·45	4·54	+0·03
	7·32	4·47	−0·04

ALLOY 3

Antimony (diff.) Per Cent.	$KMnO_4$ (1 ml. = 0·0061 g. Sb) ml.	Antimony found Per Cent.	Error Per Cent.
9·97	16·35	9·97	± 0·00
	16·40	10·00	+0·03
	16·40	10·00	+0·03
	16·30	9·94	−0·03

On varying the concentrations of hydrochloric and sulphuric acids in the proportions quoted by Pugh (*loc. cit.*) no deviation from the above results was obtained. With the higher concentrations of hydrochloric acid the end-points were quite as sharp, but the permanganate colour faded more rapidly. This error may be eliminated by titrating the solution while hot (methyl orange as indicator), the permanganate being added, drop by drop, towards the end of the titration; by this means, also, the time for one determination may be reduced to 20–30 minutes.

It appears evident, therefore, that within the limits of experimental error the method gives good results. The titration offers no difficulty, and the end-point is distinct with one drop of *N*/30 permanganate solution. Thus, with such a solution a difference of 0·05 ml. in titrations corresponds with 0·01 per cent. on 1 g. of sample, whereas with *N*/10 permanganate solution 0·05 ml. corresponds with 0·03 per cent.

ANTIMONIAL LEAD.—Four alloys, with antimony-contents ranging from 0·5 to 1·1 per cent., were examined. It had been ascertained previously that arsenic was absent, and only antimony was therefore determined. The results are shown in Table V:

TABLE V

	Antimony found		
Sample	Gravimetrically as Sb_2O_4 Per Cent.	By titration (Györy) Per Cent.	By fusion with $KHSO_4$ Per Cent.
A	1·17	1·15	1·12
B	0·95	0·91	0·92
C	0·85	0·90	0·87
D	0·53	0·53	0·50

LEAD-ANTIMONY ALLOYS CONTAINING ARSENIC.—When such alloys are dissolved in conc. sulphuric acid, arsenic behaves like antimony, being oxidised by potassium permanganate from the tervalent condition (in which form it exists in such a solution) to the quinquevalent condition, and for accurate determinations of antimony volatilisation of arsenic has been recommended.[9,10] In this investigation the volatilisation of arsenic was not attempted, and the results in Table VI show that the reaction is quantitative and that no loss of arsenic occurs either during the fusion process or subsequent operations.

In these experiments varying weights of pure arsenic were fused with potassium bisulphate and 1 g. of lead foil. The melt was extracted and, immediately prior to titration, 25 ml. of an antimonious solution (0·0496 g. of Sb) were added to facilitate oxidation of the tervalent arsenic; the exact titre of the antimonious solution was known, the excess over this being the number of ml. used by the arsenic, as is shown in Table VI.

TABLE VI

Arsenic taken g.	$KMnO_4$ (1 ml. = 0·00375 g. Sb) ml.	Arsenic found g.	Error g.
0·0080	2·25	0·0084	+0·0004
0·0055	1·50	0·0056	+0·0001
0·0072	2·00	0·0075	+0·0003
0·0108	2·95	0·0110	+0·0002

Table VII gives the results obtained with arsenic-containing lead-antimony alloys, complete analyses of which had previously been made. A correction, in terms of ml. of permanganate solution, equivalent to the arsenic-content, has been applied to the results of the actual titration.

TABLE VIIA

	Sample 1 Per Cent.	Sample 2 Per Cent.	Sample 3 Per Cent.	Sample 4 Per Cent.
Lead	87·55	88·86	89·53	88·79
Copper	0·25	0·10	0·26	0·06
Iron	0·04	0·04	0·03	0·05
Arsenic	0·34	0·31	0·25	0·37
Antimony (diff.)	11·82	10·69	9·93	10·73
—— (gravimetrically) ..	11·69 11·88	10·68 10·53	9·96 9·90	10·77 10·74
—— (Györy)	11·90 11·79	10·80 10·80	9·84 9·90	10·70 10·65
Average ..	11·82	10·70	9·90	10·71

TABLE VIIB

Antimony (by diff.) Per Cent.	$KMnO_4$ (1 ml. = 0·0061 g. Sb) ml.	$KMnO_4$ corrected for As ml.	Antimony found Per Cent.	Error Per Cent.
11·82	20·20	19·30	11·78	−0·04
10·69	18·32	17·50	10·69	± 0·00
9·93	17·00	16·33	9·96	+0·03
10·73	18·60	17·62	10·74	+0·01

It is thus evident that arsenic reacts quantitatively and that a correction must be applied to obtain the correct antimony-content.

LEAD-ANTIMONY ALLOYS CONTAINING TIN.—Tin does not interfere in the determination of antimony by Low's method, being present in the quadrivalent condition after digestion with conc. sulphuric acid. It was found that tin had no effect on the determination by the bisulphate fusion method, as regards the results obtained, but its presence tends to increase the viscosity of the melt, and in amounts greater than 50 per cent. renders fusion difficult; for such alloys it is advisable to increase the amount of potassium bisulphate to 10 g. The method is suitable for alloys with tin-contents up to 50 per cent., and results obtained with a few of the alloys examined are given in Table VIII.

TABLE VIII

Sample	Tin Per Cent.	Antimony (gravimetric) Per Cent.	Antimony (bisulphate fusion) Per Cent.	Remarks
White metal "A" (Ridsdale's Chem. Standards)	4·56	—	12·06	B.C.S. (Ridsdale's) Certified Sb 12·04 per cent.
Solder 1	49·50	2·72	2·75	
Solder 2	50·17	2·80	2·85	
Tin-foil	4·50	—	0·62	Györy titration 0·70 per cent.

Such alloys, however, are rapidly attacked by boiling conc. sulphuric acid, and with them there is probably little advantage in the modified method, which is recommended principally for lead alloys, which are attacked only with difficulty under such conditions.

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THE WOOLWICH POLYTECHNIC
LONDON, S.E.18

The Determination of Small Quantities of Copper in Iron

BY JAMES G. FIFE, B.Sc., A.I.C., AND
SYDNEY TORRANCE, A.R.C.S., B.Sc., D.I.C.

THE quantitative electrolytic deposition of copper from solutions having a high concentration of iron meets with considerable difficulty, owing to the fact that oxidation of ferrous to ferric ions takes place at the anode, and these ferric ions must be reduced to the ferrous state at the cathode before copper can be quantitatively deposited.

Two methods which have been described by Sand[1,8] suggest themselves. In the first of these the revolving anode is surrounded by a parchment diaphragm and is kept from contact with the liquid under examination. The second is the method of so-called internal electrolysis.

PART I. USE OF THE REVOLVING ANODE

The cathode employed was of the type described and used by Lindsey and Sand.[2] The potential between the anode and cathode was controlled by means of a saturated calomel electrode,[3,4,5,6,7] a neutral sodium sulphate solution being the junction liquid.

The catholyte consisted of 150 ml. of a solution containing the copper to be determined, ferrous sulphate equivalent to 10 g. of iron, 1·5 ml. of 96 per cent. sulphuric acid, and 10 ml. of a 2 per cent. solution of hydrazine sulphate.

The anolyte was a 10 per cent. solution of sodium sulphate ($Na_2SO_4.10H_2O$) plus 1 per cent. of sulphuric acid.

Electrolysis was commenced at room temperature with an auxiliary electrode to cathode P.D. of 0·4 volt, which was maintained throughout. This gives an initial current of about 0·3 amp., which falls during the course of the electrolysis to below 0·05 amp. After 15 minutes the anode was flushed out by pouring some fresh anolyte into the funnel top. The liquid in the tip of the auxiliary electrode was also flushed out, and the electrolysis was continued for a further 10 minutes, or until a drop of the catholyte gave a negative test for copper with rubeanic acid. The cathode was then removed, washed, dried and weighed.

The following results were obtained:

Copper taken g.	Copper found g.
0·0000	0·0000
0·0030	0·0029
0·0030	0·0030
0·0050	0·0050
0·0050	0·0049
0·0125	0·0125
0·0125	0·0126
0·0200	0·0199
0·0300	0·0302

PART II. DETERMINATION BY INTERNAL ELECTROLYSIS*

(STUDIES IN INTERNAL ELECTROLYSIS. II)

The apparatus used was that described by Sand[9] with the modifications used in the determination of small proportions of cadmium and of nickel in zinc.[10] The anodes in this case consisted of iron wire about 1 mm. in diameter.

It was found that small quantities of copper could be determined in the presence of large quantities of iron by the method of internal electrolysis, provided that sufficient acid was present to keep the solution clear and that the iron was all present in the ferrous state.

Satisfactory results were obtained by the use of an anolyte containing ferrous sulphate equivalent to 5 g. of iron, 3 ml. of 96 per cent. sulphuric acid and 0·2 g. of hydrazine sulphate per 100 ml., and a catholyte of approximately 300 ml. containing the copper to be determined, ferrous sulphate equivalent to 5 g. of iron, 0·2 g. of hydrazine sulphate and 3 ml. of 96 per cent. sulphuric acid.

The results are shown in Table I.

TABLE I

No. of Expt.	Copper added g.	Copper found g.	Time of electrolysis Minutes
1	0·0030	0·0031	30
2	0·0060	0·0060	32
3	0·0100	0·0100	30
4	0·0150	0·0150	33
5	0·0300	0·0295	34
6	0·0075	0·0074	30
7	0·0060	0·0060	30
8	0·0015	0·0015	30
9	0·0050	0·0050	30
10	0·0100	0·0101	30
11	0·0200	0·0198	45
12	0·0300	0·0300	40
13	0·0010	0·0011	30
14	0·0025	0·0025	30
15	0·0250	0·0249	40
16	0·0125	0·0124	30
17	0·0040	0·0040	20
17*a*	*nil*	*nil*	25

In every instance the electrolysis was carried out at approximately 70° C.

In Expts. 4 and 5 the electrolysis was continued until constant weight was obtained, thus proving that a prolongation of the experiment has no harmful effect.

Furthermore, in Expts. 1 to 5 the catholyte, in addition to the substances mentioned above, contained 3 g. of ammonium sulphate and the anolyte contained 1 g. of ammonium sulphate per 100 ml., whilst in Expt. 7 sodium chloride (1 g.) was added to the catholyte.

The method was next applied to the determination of copper in steels, and the procedure recommended is as follows:

The steel (about 3 to 10 g., according to the amount of copper present) is dissolved in sulphuric acid in an atmosphere of carbon dioxide—for example, by the use of a Contat-Göckel valve,[11] the solution is cooled, filtered and neutralised with caustic soda or ammonia, and 3 ml. of 96 per cent. sulphuric acid and sufficient hydrazine or hydroxylamine sulphate to convert any ferric to ferrous ions and leave a small amount of free hydrazine or hydroxylamine sulphate are added. It is advisable to ensure the absence of ferric ions by means of a test with ammonium thiocyanate. The solution is then diluted to about 300 ml., and electrolysed at approximately 70° C. as described, the composition of the anolyte being the same as in the previous experiments.

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* The first record of an attempt to determine copper by a method of internal electrolysis is in a paper by Ullgren.[8]

Results are shown in Table II (Expt. 18) for a plain carbon steel, and also (Expts. 19 to 21) for "Bearco," a steel containing copper and recommended for use in parts subject to corrosion.

TABLE II

No. of Expt.	Steel taken g.	Copper found g.	Copper Per Cent.
18	6·09	0·0007	0·01
19	3·20	0·0045	0·14
20	1·02	0·0015	0·15
21	1·28	0·0018	0·14

Expts. 18 and 20 were continued until constant weight was obtained. In Expt. 19 the residue from the filtration was extracted with hot dilute nitric acid, and the extract was tested for copper by means of rubeanic acid, but with a negative result. The residue from the nitric acid extraction was ignited to burn off the carbon, and then dissolved in nitric acid, and the solution was tested for copper as before, but again with a negative result.

Moreover, in Expts. 18 and 21 known amounts of copper were added to the catholyte after the determination, and a further determination was made. In each instance the weight of the deposit was the same as that of the copper added, thus confirming the correctness of the method.

We wish to thank Dr. Sand for his interest in this work.

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THE SIR JOHN CASS TECHNICAL INSTITUTE
LONDON, E.C.3.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

AN ANALYSIS OF BANANA OIL

In the course of a metabolism experiment on lemurs, fed chiefly on bananas, it became of importance to have some knowledge of the composition of the fatty constituents which, in a series of five analyses, were found to account for from 0·72 to 0·8 per cent. of the dry weight of the fruit. No information regarding the probable composition of this material was traced in the literature.

Thirty peeled bananas, just fit for eating, were dehydrated by grinding with anhydrous sodium sulphate and extracted with ether. The solvent was removed from the extract, and the residue was extracted with petroleum spirit (b.p. 40°–60° C.). Two g. of a dark brown, rather viscous oil were obtained. A small amount of a waxy crystalline material separated out on standing a few days, but the amount was too small for fractionation.

The following results were obtained on examination of the oil:

Refractive index, n_D^{40}	1·4648
Iodine value	82
Unsaponifiable matter	14·4 per cent.
Sterol precipitable by digitonin	30·6 per cent. of unsaponifiable matter
Mean mol. equiv. of fatty acids	286
Iodine value of fatty acids	90

The sterol, precipitated as digitonide, was isolated by extraction with hot xylene. After several recrystallisations from methyl alcohol a product was obtained with m.p. 135° C. and $[\alpha]_D^{20}$ (benzene) 20·0°. It yielded an acetate, m.p. 124° C. It was probably a sitosterol.

The residue of the unsaponifiable fraction, after removal of the sterol by digitonin, was freed from excess of the precipitant and dissolved in petroleum spirit (b.p. 40°–60° C.), and the solution was poured through a column of adsorbent aluminium oxide. Nearly 70 per cent. passed through unadsorbed. This material—a colourless, viscous oil (iodine value 37)—represents the hydrocarbons. The amount was insufficient for an attempt at separation to be made.

The remaining 30 per cent. of the sterol-free unsaponifiable matter, which was adsorbed, was probably of the nature of saturated alcohols.

The fatty acid fraction was too small in amount to fractionate, but a superficial examination suggested that it was of the common stearic-palmitic-oleic type.

A. R. Moss

Biochemical Department
University College
London, W.C.1

SPECTROGRAPHIC ANALYSIS OF PAINT

The present note on the application of spectrographic analysis, although recording negative results, was considered worthy of record in order to save possible duplication by future workers in the same field.

The problem originally approached was concerned with the possibility of the application of spectrographic methods to the determination of the proportions of toxic components, *viz.* arsenic, mercury, copper and lead, in paints and compositions such as are employed as antifouling coatings for the hulls of ships.

Although determinations to an accuracy of only 10 per cent. of the true figures were in view, the results of the work here described indicate that to obtain even such a rough estimate as this is by no means a simple matter.

Quantitative spectrographic analysis has been most successful in its application to metals, and, at the time of the present work was soundly established in this respect, especially when applied to the determination of minor ingredients. The technique of such work is well known and widely described in the literature and is based on internal relation with elements present in higher proportions.

The outstanding point with regard to metallurgical spectroscopy is that a homogeneous conducting material is being dealt with, and the progress made has been largely due to this.

As applied to paints the problem presented a different aspect. The material, being a non-conductor, had obviously to be burnt in a carbon arc, and it was soon realised that the more volatile constituents would burn away and volatilise before the more refractory ones had been materially affected. It appeared, therefore, to be essential that the paint should be burnt to completion in the arc during the period of spectrographic examination.

Owing to the ready volatility of the arsenic and mercury compounds in the paints under examination it was feared that a proportion of these metals might volatilise before a steady arc was established, and, in order to avoid this, preliminary tests were carried out in which cavities were drilled in a number of carbon electrodes and small quantities of dried paint inserted therein. On the first electrode this paint layer was covered with a layer of carbon black, on the second electrode with a layer of graphite, on the third with a layer of ammonium sulphate, and on the fourth with a well-fitting carbon disc. These were burnt in the arc, and, as it was found that the layer of ammonium sulphate was the most satisfactory, it was adopted for most of the subsequent work, since it possessed the dual effect of delaying the volatilisation of the paint until the formation of a constant arc, and of increasing the conductivity of the paint (*cf.* Lewis, ANALYST, 1935, **60**, 10).

The employment of the dried paint in preference to the material in its original state was found to be advantageous in minimising the volume of black smoke evolved. Although the presence of carbonaceous matter in material to be spectrographed is deprecated by some workers, it is obvious that the complete elimination of organic matter in this instance could only be accomplished by protracted chemical methods, which would unduly prolong the preliminary treatment.

A series of antifouling paints containing varying percentages of toxic metals were selected for the test; a typical paint contained 8·7 per cent. of copper, 16·8 per cent. of arsenic (as As_2O_3) and 7·2 per cent. of mercury. These were burnt in a graphite arc, and the intensities of suitable spectrographic lines were compared with those obtained by burning a second series of paints similar to the first series, with the exception that the contents of toxic metals had been increased by 10 per cent. of their previous values. Comparison was also carried out with a third series of paints in which the percentages of the toxic metals had been decreased by 10 per cent., as compared with the first series.

In each instance the same weight of paint was used and the material was burnt to completion, while all controllable conditions, *e.g.* arc gap, slit-width, electrical current and potential, time of exposure, etc., were maintained constant. As an example, 20 mg. of the dried paint required about 3 minutes' exposure with a current of 4 amps. and a voltage of 200. Both the large and medium dispersion quartz spectrographs of Messrs. Hilgers were employed.

It was found, after comparison of the various spectrographs, that no consistent or reproducible comparative line intensity could be obtained corresponding with the 10 per cent. variation of the contents of toxic metals.

The effect of increasing the amount of paint consumed, with a relative increase in the distance from the spectrographic slit was also tried, as was also the effect of omitting the covering layer of ammonium sulphate, but again with negative results.

Further tests were undertaken in which the paints were diluted with zinc oxide, in order relatively to reduce the percentage of toxic metals present, and, also, to enable the method of internal comparison with the zinc lines to be employed. In this case, too, correlation could not be obtained, although it is recognised that under laboratory conditions an intimate, homogeneous mixture of zinc oxide and paint is difficult to obtain.

An apparently promising sideline of the investigation was the employment of spectrographic analysis for the determination of small amounts of lead in paints required to be free from lead. For this purpose the organic matter was eliminated from the paints by ashing them at 500° C., and the resulting ash was burnt in the arc and spectrographed. There has, as yet, been no opportunity of pursuing this investigation further, but the preliminary results obtained were encouraging in paints containing traces of lead of the order of 0·05 per cent. and below.

We wish to acknowledge our indebtedness to the Admiralty for having given permission to publish this note.

F. H. NEWINGTON
C. D. LAWRENCE

DEPARTMENT OF THE ADMIRALTY CHEMIST
H.M. DOCKYARD
PORTSMOUTH

Official Appointments

THE Minister of Health has approved the following appointments:

ALEXANDER MITCHELL MUTER as a Public Analyst for the Administrative County of the Parts of Holland, Lincolnshire, in place of B. H. Gerrans (deceased) (November 26th, 1936).

REGINALD FRANK WRIGHT as a Public Analyst for the County Borough of Brighton, in addition to Samuel Allinson Woodhead (November 10th, 1936).

REGINALD FRANK WRIGHT as a Public Analyst for the County Borough of Eastbourne, in addition to Samuel Allinson Woodhead (November 10th, 1936).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

CITY ANALYST'S REPORT FOR THE YEAR 1935

OF the 6241 samples examined, 5464 were taken in connection with the Sale of Food and Drugs Act, 271 being formal and 5193 informal samples.

DAILY VARIATIONS IN FREEZING-POINT OF MILK.—With the co-operation of the farmers concerned, a series of tests was made, during March and April, 1935, of the milk from four different sources, with the object of determining to what extent the freezing-point depression varied from day to day, and also from morning to afternoon. The samples were taken each day for a period of three weeks from the churns received at a depot in the City. Farmer No. 1 milked 25 Shorthorn cows of ages varying from 4 to 8 years at intervals of 10 and 14 hours. Farmer No. 2 sent milk from 19 Shorthorn cows, from 3 to 8 years old, milked at intervals of 10¼ and 13¾ hours. The milk sent by Farmer No. 3 came from 10 cows milked at intervals of 10 and 14 hours, and that sent by Farmer No. 4 from 9 cows (2½ to 6 years old) from March 31st to April 11th, and from 10 cows from April 12th to April 17th, milked at intervals of 10¾ and 13¼ hours.

The range of freezing-point depressions was as follows:

Farmer	I	II	III	IV
Freezing-point depression	0·534 to 0·557	0·533 to 0·562	0·541 to 0·559	0·535 to 0·556

The range was 0·029, or, expressed as a percentage of the higher figure, 5·2 per cent. The solids-not-fat varied from 8·2 to 9·1 per cent., or expressed as a percentage of the higher figure, 9·9 per cent.

The greatest day-to-day variation of the freezing-point depression was 0·017, whilst the greatest day-to-day variation in solids-not-fat was 0·5. The samples of milk received from Farmer No. 3 contained less than 8·5 per cent. of solids-not-fat on 12 occasions. In no instance, however, did the freezing-point depression fall below 0·541, showing that the low solids-not-fat figures were the results of natural variation in composition.

Dried Mint.—One of two samples examined contained 6 per cent. of extraneous mineral matter. The packers stated that it was very difficult to remove mineral matter completely, and that, owing to its weight it had sunk to the bottom of the consignment of mint, so that the last few packets had received nearly all of it.

Sild in Olive Oil.—Two samples of Norwegian origin contained 5·3 and 5·4 grains of tin per lb., and the cans were badly corroded.

"Non-Tannic" Tea.—One of 16 samples of tea examined was labelled "non-tannic and free from all stalk which contained crude tannin," and "Digestive because non-tannic." The amount of tannin actually present was 16 per cent., a rather higher figure than the average. The firm agreed to remove the reference to tannin from their labels. As the result of action taken with regard to so-called "Digestive" teas, very few of such teas are now sold. In the past six years no fewer than 16 packers have been cautioned and have agreed to revise labels containing misleading references to the tannin-content.

Lemon Vinegar.—A sample of so-called "lemon vinegar" had an acidity of 5·2 per cent. and contained a small quantity of oil of lemon.

"Vinegar Acid."—A sample bearing this name was nearly pure dilute acetic acid (21·6 per cent.). It was apparently intended to be diluted and coloured to produce artificial vinegar.

H. H. Bagnall

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ADULTERATION AND MISDESCRIPTION OF SEA SALT*

This case relates to a consignment of sea salt, sold in the United States under a proprietary name, and represented, in violation of the U.S.A. Food and Drugs Act, to consist of salts obtained by the direct evaporation of sea water. Analysis of a sample showed it to contain 98·3 per cent. of sodium chloride, 0·25 per cent. of calcium salts (as CaO), and traces of magnesium and sulphate compounds.

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* Notice of Judgment under the Food and Drugs Act, No. 25031, U.S. Dept. of Agriculture, Washington, D.C. (July, 1936).

The article was alleged to be adulterated, in that its strength fell below the professed strength and quality under which it was sold, namely, "Sea Salt . . ." "This Salt being extracted directly from sea water by evaporation."

Misdescription was also alleged for the reason that the following statements appearing on the label were false and misleading:—"——'s Sea Salt for producing a Real Sea Bath at Home." "Purified Sea Salt for Producing Real Sea Salt Water at Home. By dissolving six ounces (or about an ordinary coffee cupful) of this Salt in one gallon of ordinary water."

The product was condemned, and no claimant having appeared, its destruction was ordered by the Court.

Analytical Methods Committee

SUB-COMMITTEE ON METHODS OF SOAP ANALYSIS

REPORT No. 3

THE DETERMINATION OF FREE ALKALI IN SOAPS

In 1931 the Analytical Methods Committee of the Society appointed a Sub-Committee to enquire into methods for the determination of unsaponifiable matter in oils and of unsaponified fat in soaps. This Sub-Committee issued two Reports: No. 1, dealing with the determination of unsaponifiable matter in oils; No. 2, with unsaponified fat in soaps. During 1935 the Analytical Methods Committee resolved that the Sub-Committee should be re-named the Sub-Committee on Methods of Soap Analysis, and that it should examine methods for soap analysis in such order as it should itself consider desirable.

Accordingly, methods for the determination of free alkali (hydroxide and carbonate) have been studied. The Sub-Committee has met eight times, and its members have carried out much experimental work with the object of discovering the best methods available and their applicability to commercial soaps. The personnel of the Sub-Committee is as under, and it now presents Report No. 3, on the Determination of Free Alkali in Soaps.

SUB-COMMITTEE

Nominated by the Government Chemist.—F. R. Ennos, B.A., B.Sc., F.I.C.

Nominated by the London Chamber of Commerce and Messrs. Unilever, Ltd.—B. D. W. Luff, F.I.C.

Nominated by the London Oil and Tallow Trades Association.—E. R. Bolton, M.I.Chem.E., F.I.C.

Nominated by the Society of Public Analysts and Other Analytical Chemists.—H. E. Cox, D.Sc., Ph.D., F.I.C. (Chairman), D. E. Davis, B.Sc., F.I.C., W. H. Simmons, B.Sc., F.I.C., and N. Evers, B.Sc., F.I.C. (Hon. Sec.).

THE DETERMINATION OF FREE ALKALI IN SOAPS

The free alkali in soaps is usually made up of hydroxide and carbonate of sodium or potassium or of both. Alkalinity may also be due to the presence of sodium silicate or other alkaline compounds which may be added to the soap; it is the usual practice to include such alkalinity as "carbonate alkali."

Methods are available for the determination of the "total free alkali," for "free caustic (or "hydroxide") alkali," and for "carbonate alkali." When any two of these figures have been determined, the third can be calculated.

The methods recommended in this report apply to most ordinary soaps. They cannot always be applied, without some modification, to special types, such as silicated or medicated soaps.

METHODS EXAMINED.—The following list includes the more important of the previously published methods to which we have given attention. It does not pretend to be an exhaustive bibliography of the subject.

(1) *The Determination of Total Free Alkali.*
Vizern and Guillot (*Ann. Chim. anal.*, 1934, **16**, 446).

(2) *The Determination of Free Caustic Alkali.*

(*a*) The method of the British Pharmacopoeia, 1932.
(*b*) The standard method of the American Oil Chemists' Society (*Oil and Soap*, 1934, **11**, 90).
(*c*) The standard method of the German Soap Manufacturers' Association (Wizoff, *Wissenschäftliche Zentral Stelle für Oel und Fett Forschung*).
(*d*) Vizern and Guillot's method (*loc. cit.*).
(*e*) Poethke's method (*Fettchem. Umschau*, 1935, **42**, 180–182, 197–201).
(*f*) Methods using barium chloride, *e.g.*
Report No. T.G.23, Govt. Dept. Specifications for General Stores. Soaps. 1929.
Heermann (*Chem.-Ztg.*, 1904, **28**, 53 and 60) (Abst., ANALYST, 1904, 129).
Ismalsky (*Deutsch. Oel und Fettind.*, 1926, **46**, 545–6, 562–4).
Kling, Gonin and Florentin (*Bull. Soc. Chim.*, 1914, 200).
Hetzer (*Fettchem. Umschau*, 1935, 87).
(*g*) Methods depending on salting-out the soap followed by titration using silver nitrate as an indicator (Newington, *J.S.C.I.*, 1916, **35**, 95).
(*h*) Davidson (*Chem. Umschau*, 1926, 273).

(3) *The Determination of Carbonate.*—The published methods nearly all depend on the assumed alcohol insolubility of the carbonate and the titration of the residue. In some cases the determination of carbon dioxide is recommended, *e.g.* in the method of the American Oil Chemists' Society (*loc. cit.*). Vizern and Guillot (*loc. cit.*) suggest titrating the free caustic alkali in strong alcoholic solution, then diluting with water to 50 per cent. strength and titrating the carbonate.

I. DETERMINATION OF TOTAL FREE ALKALI

This may be carried out by adding to an alcoholic solution of the soap slightly more mineral acid than is sufficient to neutralise the free alkali. After heating to remove carbon dioxide the liquid is titrated back with alkali using phenolphthalein as indicator. Vizern and Guillot (*loc. cit.*) suggest the use of an alcoholic solution of fatty acids instead of a mineral acid, stating that errors may be introduced by esterification of the liberated fatty acids in the acid alcoholic solution and by the re-formation of anhydrides when the soap is decomposed by mineral acid. A careful comparison has indicated no significant difference between the results obtained by the two methods, and we have not been able to find any evidence of the presence of anhydrides or lactones. On grounds of convenience, therefore, we recommend the use of mineral acid.

RECOMMENDED PROCEDURE.—Boil 100 ml. of re-distilled industrial methylated spirit (66 o.p.)* in a 400-ml. flask, add 0·5 ml. of a 0·5 per cent. alcoholic solution of phenolphthalein, allow to cool to 70° C. and neutralise at that temperature with 0·1 *N* alcoholic potassium hydroxide solution. Add 10 g. of the soap in thin shavings and dissolve it as quickly as possible by heating. Immediately after complete solution of the soap add 3 ml. of *N* sulphuric acid and boil on a water-bath for at least ten minutes to ensure complete removal of carbon dioxide. If the solution is colourless, cool to 70° C. and titrate back with *N* sodium hydroxide until the pink colour reappears. If, after the boiling with acid, the pink colour returns, a further quantity of *N* sulphuric acid must be added and the boiling repeated, the titration being completed as described above. The excess of *N* sulphuric acid titrated should be not less than 1 ml. From the amount of standard acid absorbed calculate the total free alkali in terms of Na_2O (or of K_2O in the case of a potassium soap).

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* *I.e.* 94·7 per cent. by volume.

The results in the following table were obtained by members of the Sub-Committee by this method on the same sample of soap.

Observer.	Total free alkali as Na_2O Per Cent.
A	0·49
	0·48
	0·49
B	0·50
	0·50
C	0·48
	0·50
D	0·48
	0·48
E	0·45
	0·48
	0·48

II. THE DETERMINATION OF FREE CAUSTIC (HYDROXIDE) ALKALI

(*a*) DIRECT TITRATION WITHOUT THE ADDITION OF BARIUM CHLORIDE.—The solubilities of sodium and potassium carbonates in alcohol of 90 per cent. strength and over at 70° C. were determined in order to assess the error likely to be introduced by this factor into direct titration methods. The results showed that, whereas the solubility of sodium carbonate is slight and may be neglected if the soap is dissolved in alcohol of 95 per cent. strength or over, potassium carbonate is sufficiently soluble in all strengths of alcohol to introduce serious errors. Direct titration methods for potassium soaps are therefore excluded, and further work on these methods was confined to sodium soaps.

The addition of anhydrous sodium sulphate or the use of absolute alcohol in order to reduce the solubility of carbonates was found to have no advantages. Salting-out methods such as that of Newington (*loc. cit.*) did not, in our hands, give satisfactory results.

All the experiments with direct titration methods were carried out under conditions similar to those recommended in Report No. 2 for the determination of free fatty acids.

Quantity of soap to be used.—In most cases a quantity of 10 g. is to be preferred. There is little advantage to be gained by using larger amounts, whilst, if the quantity is less, the errors of the method may be of significant magnitude.

Solvent.—The best solvent is industrial alcohol of about 95 per cent. strength. The use of stronger alcohol makes it difficult to dissolve the soap. A mixture of isopropyl alcohol and glycol as recommended by Poethke (*loc. cit.*) involved many corrections and was not considered likely to repay further investigation.

Filtration.—We find that it is very difficult to effect filtration of a soap solution containing small quantities of free caustic alkali without incurring some loss of hydroxide. Investigation showed that this is due largely to absorption of atmospheric carbon dioxide. As it is possible to titrate the hydroxide alkali without filtration, we recommend that filtration should be abandoned.

Conclusions.—We find that the method of direct titration without filtration may be used satisfactorily in the absence of much carbonate. In the presence of carbonate the end-point is not sharp, and the results on sodium soaps tend to be slightly high, and on potassium soaps very high. The method is recommended only for sodium soaps and in the absence of more than about 0·4 per cent. of total free alkali calculated as Na_2O.

Procedure.—Boil 100 ml. of industrial alcohol (66 o.p.) to remove carbon dioxide. Add 0·5 ml. of 0·5 per cent. solution of phenolphthalein and neutralise at 70° C. with 0·1 *N* acid or alkali. Add 10 g. of the soap in shavings or powder and heat until dissolved. Cool to 70° C. and titrate at that temperature with 0·1 *N* sulphuric acid.

(*b*) DIRECT TITRATION AFTER THE ADDITION OF BARIUM CHLORIDE.—When more than about 0·4 per cent. of total free alkali is present, it is necessary to remove this with barium chloride. The addition of barium chloride to an alcoholic solution of a soap neutral to phenolphthalein causes the reaction to become slightly acid, probably owing to the precipitation of a basic barium compound. Consequently the results obtained for free caustic alkali by this method tend to be low. The error due to this cause may be reduced by increasing the weight of soap taken and by keeping the quantity of barium chloride as low as possible.

This method is recommended to be applied to soaps containing any potash or more than 0·4 per cent. of total free alkali.

Recommended procedure.—Dissolve 10 g. of the soap in 100 ml. of neutral industrial alcohol containing 0·5 ml. of 0·5 per cent. solution of phenolphthalein. Add 5 ml. of hot neutral 10 per cent. aqueous solution of barium chloride in a thin stream, mix thoroughly, and titrate with 0·1 *N* hydrochloric acid at 70° C. until the pink colour disappears.

The following table shows the margin of error obtained with known amounts of caustic alkali added with or without the addition of sodium carbonate to a neutral soap solution.

Observer	Weight of soap g.	10 per cent. $BaCl_2$ solution ml.	2·5 per cent. Na_2CO_3 solution ml.	Caustic alkali as Na_2O	
				Added Per Cent.	Found Per Cent.
A	25	0	0	0·061	0·059
	25	5	0	0·062	0·053
	25	10	0	0·061	0·054
	25	25	0	0·062	0·053
	25	5	1·0	0·062	0·051
	25	5	3·0	0·062	0·050
	25	10	3·0	0·063	0·053
B	25	0	0	0·061	0·060
	25	5	0	0·061	0·055
	25	10	0	0·061	0·053
	25	10	(1 ml. satd. soln.)	0·061	0·054
	25	5	0	0·012	0·007
	25	5	0	0·024	0·018

It will be seen that the error introduced is of the order of 0·008 per cent. as Na_2O. Experiments showed that the results obtained by using 25 g. of soap were not different from those obtained with 10 g.; 10 g. quantities are preferred because solution is more difficult to effect with the larger quantity. The following table shows the agreement between different observers on different samples of the same soap using this method.

Observer	Free caustic alkali as Na_2O Per Cent.
A	0·075
	0·072
B	0·09
	0·09
C	0·099
	0·099
D	0·08
E	0·084
	0·086
F	0·09
	0·09

III. THE DETERMINATION OF FREE "CARBONATE" ALKALI

RECOMMENDED PROCEDURE (FOR SODIUM SOAPS ONLY).—Boil 100 ml. of neutral redistilled industrial methylated spirit (66 o.p.) in a 400-ml. conical flask, add 10 g. of the soap in thin shavings, and dissolve it as quickly as possible by heating. Filter rapidly while hot and wash the residue on the paper with hot alcohol until it is free from soap. Extract the residue with hot distilled water until the washings are no longer alkaline. Titrate the combined aqueous washings with 0·1 *N* hydrochloric acid, using methyl orange as indicator. Calculate the result as Na_2O per cent.

The determination of the alkalinity actually due to carbonate may be carried out by an estimation of carbon dioxide, for which any of the recognised methods may be used. This is the only direct method for carbonate alkali applicable to potassium soaps. Experiments carried out by members of the Sub-Committee have shown that for soda soaps in the absence of other interfering substances, *e.g.* alkali silicates, the results from carbon dioxide determination agree with those obtained by titration of the alcohol-insoluble matter. The method of Vizern and Guillot (*loc. cit.*) of titration in 50 per cent. alcoholic solution after the titration of free caustic alkali was not satisfactory, owing to the indefinite end-point of the first titration.

The following results were obtained by members of the Sub-Committee on a sample of soap containing a quantity of carbonate alkali and some caustic alkali.

	Carbonate alkali as Na_2O	
Observer	By filtration as above Per Cent.	By estimation of CO_2 Per Cent.
A	0·42	0·39
B	0·38	0·37
	0·41	0·39
C	0·41	—
D	0·41	—
E	0·42	—

SUMMARY OF RECOMMENDATIONS

SODIUM SOAPS.—The best procedure is to determine (1) the total free alkali by adding excess of mineral acid and titrating back with standard alkali; (2) caustic alkali by one of the methods described above. "Carbonate" alkali (3) may be found by difference between (1) and (2) and may be checked by the determination of alcohol-insoluble alkali or of carbon dioxide.

The results of all tests on hard soaps should be expressed as percentage of Na_2O.

Potassium Soaps.—Direct determination of the carbonate by a titration method is not practicable. The total free alkali (1) should be determined as in sodium soaps, free caustic alkali (2) should be determined by the barium chloride method (which is recognised as giving slightly low results). The carbonate alkali (3) is given by difference or may be determined as carbon dioxide.

The results of all tests on soft soaps should be expressed as percentage of K_2O.

These methods cannot always be applied without modification to silicated or medicated soaps.

(*Signed*) H. E. Cox (*Chairman*)
N. Evers (*Hon. Secretary*)

November 30*th*, 1936

Department of Scientific and Industrial Research

THE ANALYSIS OF COMMERCIAL LUBRICATING OILS BY PHYSICAL METHODS*

In the new edition of this Report the subject-matter has been revised without substantial alteration, and Parts I and II have been re-arranged to secure clearer presentation. The Introduction, originally written by the late Sir William Hardy, has been revised by Miss M. E. Nottage. The object of the investigation was to discover whether the method used for the measurement of friction at the boundary layer could be applied to the analysis of commercial lubricating oils.

The experimental method was as follows:—The cleaned bearing surfaces (consisting of a plane plate and a spherical slider) were lubricated with the oil to be tested, and the coefficient of static friction at the boundary layer was measured when the system (*i.e.* bearing surfaces + oil) was heated to different temperatures between 18° C. and 110° C., and in the two atmospheres, air and nitrogen. From the results so obtained friction-temperature curves were plotted. A detailed description of the apparatus used is given in Appendix I.

Part I gives the facts established by the investigation relating to the change in the lubricating value of a commercial oil, produced by passing it over an adsorbing surface. It is shown that the power to recover the original lubricating value after percolation is possessed by some oils, but not by others; such recovery is a comparatively slow process, and is dependent upon the presence of air. This section also contains a study of the friction-temperature curves of oils of known composition under varying concentrations of (*a*) non-polar constituents (wax and normal paraffins), and (*b*) polar constituents. As a diluent it was necessary to use a substance which itself showed no variation of friction with temperature, and this was found in the medicinal paraffin of the British Pharmacopoeia.

Part II deals with physical analysis, and is based upon the study of lubricants of known compositions, *e.g.* mixtures of paraffin wax, B.P. oil and palmitic acid. The sub-section on "Reversibility" in this Part has been considerably condensed, as later work appears to suggest that much more information is needed before hypotheses as to the mechanics of the changes occurring can be formulated.

Part III, by Miss Nottage, on "Chemical Possibilities," reviews the properties of the chief classes of substances known to be present in lubricating oils, and attempts to correlate these substances with the hypothetical constituents, the presence of which was deduced from the physical analysis of the curves. The substances discussed include:—(i) the unsaturated hydrocarbons of both the open- and closed-chain series; (ii) the asphaltic and resinous substances; and (iii) paraffin wax. The results of fractionating oils of known composition are also discussed.

There are 22 references to the literature of the subject, dating from 1877 to 1934.

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* Lubrication Research. Technical Paper No. 1. 2nd Ed., pp. 52. London: H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1936. Price 1s. net.

New Zealand

Department of Agriculture

ANNUAL REPORT OF THE CHEMISTRY SECTION FOR 1935–1936

THE Annual Report of the Chief Chemist (Mr. B. C. Aston, F.I.C.) forms a section of the main Report of the Director-General of the Department of Agriculture, which is a record of the work of the Department in promoting the efficiency and development of rural industries. The work of the Chemistry Section has included the examination of materials for other Departments, such as analyses of toxicological specimens, licks, wool-scouring materials, soils, fertilisers, waters, bloods, etc. The total number of samples examined was 994, of which 434 were specimens of blood and 145 were soils. The scientific investigations on the deficiency diseases of live-stock have been continued, but, as regards bush sickness in ruminants, have now become almost entirely academic in character.

USE OF METAL SALTS IN BUSH SICKNESS.—Whilst metallic salts other than those of iron (*e.g.* arsenic) are capable of curing bush sickness in individual ruminants, there is no proof that any element, except iron, known to be essential for nutrition, will prevent bush sickness in a series of generations as iron salts do. A deposit of soft, high-grade limonite at Maketu, Bay of Plenty, was found to have the very high solubility figure of 12·5 per cent. of ferric oxide in the special sugar and hydrochloric acid reagent, as compared with 2·4 per cent. in good Ruatangata limonite.

Zinc and Cobalt in Limonite.—In view of the importance now attached, in animal health and nutrition, to traces of elements, various limonite samples were examined for the content of zinc and cobalt soluble in *N*/10 hydrochloric acid, and the following results were obtained:

Limonite	Zinc p.p.m.	Cobalt p.p.m.
Ruatangata (highly effective)	3·0 to 3·3	5·9
Okaihau (good, but variable in effect) ..	0·0 to 2·8	1·0 to 3·4
Puhipuli (ineffective)	0·0 to 1·7	0·1 to 1·8

Samples of iron and ammonium citrate contained from nil to 50 p.p.m. of zinc and from 6·8 to 8·6 p.p.m. of cobalt. At the recognised daily dosage this would provide less than 0·015 mg. of cobalt per sheep.

Cobalt in Soils.—Samples of soil from ten different districts yielded, on extraction with *N*/10 hydrochloric acid, from 0·05 to 0·94 (average 0·67) p.p.m. of cobalt, calculated on the dry weights of soil. Elvehjem has pointed out that Fischer and Scott (*Biochem. J.*, 1935, **19**, 1055) failed to detect cobalt in the pancreas of cattle of any age, and that they place cobalt in the realm of pharmacology and toxicology rather than of nutrition.

Zinc and Cobalt in Pasture Samples.—Cocksfoot grass from Kaharoa (bush-sick area) contained 38 p.p.m. of zinc, whilst a sample from Northland, Wellington, contained 32 p.p.m.

Cobalt could not be detected in several samples of pasture from both sick and healthy areas. It would therefore appear that cobalt is not taken up from the soil in appreciable quantities by pasture, and that the good results in preventing bush sickness which are obtained by giving a top dressing of ferrous sulphate to pasture are probably due to increased absorption of iron from the soil by the pasture.

Zinc and Cobalt in Animal Specimens.—No cobalt was found in the pancreas of a healthy bullock. Traces were present in the testes of healthy rams and bulls (less than 0·2 p.p.m. of the dry material). The livers of bush-sick sheep showed faint traces of cobalt (about 0·06 p.p.m.), as compared with 0·20 p.p.m. in a healthy sheep. Less than 0·06 p.p.m. was found in the brain of a healthy sheep.

The zinc-content of testes of healthy rams from bush-sick areas ranged from nil to 43·9 p.p.m. of dry tissue, as against 64·0 to 80·8 p.p.m. for rams from healthy areas. The liver of a sick sheep from the bush-sick area contained 140·8 p.p.m. of zinc in the dry tissue, as compared with 254·6 p.p.m. in the liver of a healthy Wellington sheep.

Ionisable Iron in Pastures.—The available or ionisable iron in bush-sick and healthy pastures and root crops is being determined by the dipyridyl method. Eleven p.p.m., on the dry substance, were found in cocksfoot grass from Kaharoa (bush-sick) and 7 to 11 p.p.m. in cocksfoot grass from Wellington. The liver of a bush-sick sheep contained 151·8 p.p.m. of total iron (soluble inorganic and organically combined), as compared with 234·1 p.p.m. in a Wellington (healthy) liver. In this case, therefore, there was no evidence of storage of excess of iron in the liver owing to non-utilisation, as is stated to occur in enzootic marasmus.

Tests for Vanadium in Limonite.—Special tests for vanadium in acid extracts of limonite were made, but none was found.

Micro-methods for Cobalt and Zinc.—It was found that the most suitable method for the micro-determination of cobalt was by the use of nitroso R-salt, and a standard procedure, involving the separation of iron, was evolved, whereby amounts down to 0·001 mg. could be determined. After trials of various methods the oxalate and ferrocyanide turbidity method of Hibbard was adopted for the determination of zinc.

Blood Analyses and Field Experiments.—Sheep from bush-sick areas were given limonites, iron and ammonium citrate, Kenya iron oxide, and copper sulphate, and samples of their blood were analysed at fortnightly intervals. It was found that the variations for total iron and total solids of each sheep were similar, showing a definite relationship. These values also increased as the health of the animal improved. The non-haemoglobin iron was a small fraction of the total iron and seemed to have no significant connection with the health of the animal. The values for total solids varied from 12 to 22 g. per 100 ml., and those for total iron from 20 to 48 mg. per 100 ml. The total iron in normal healthy blood averaged 49·4 mg. per 100 ml.

The copper-content of the blood of sick sheep was 0·093 to 0·16 mg. per 100 ml., whilst the values for healthy sheep in the same district varied from 0·083 to 0·160 mg. per 100 ml., so that the copper figures have no clinical value. The sheep fed on copper sulphate gave an average value of 0·148 mg. per 100 ml.

To summarise the position, it would seem to be the wisest course for farmers to continue to use approved limonite as a stock lick.

ANALYSES OF PAMPAS GRASS.—It was found that the succulent leaf-bases of *Cortaderia selloana*, which are greatly relished by cattle, contained only 14·1 per cent. of lignin in the dry substance, as compared with 20·1 to 21·5 per cent. in the dry matter of the green leaf-blade. Analyses of samples from a row of pampas grass, transplanted as seedlings, gave the following results:

	Total hemi-celluloses	Pectic substances	Lignin	Cellulose (C and B)	Reducing sugars Before hydrolysis	Reducing sugars After hydrolysis	Protein	Ash	P_2O_5	Calcium oxide
Dec. 24, 1935	24·2	0·53	20·5	45·5	0·82	1·01	8·58	6·88	0·34	0·31
Mar. 12, 1936	27·2	0·56	20·6	39·6	2·17	5·06	11·52	8·75	0·32	0·31

ACTIVE PRINCIPLES OF NEW ZEALAND PLANTS.—The poisonous tutu plant (*Coriaria* sp.) from which the active principle tutin was isolated in 1900, may come into pharmacological importance, owing to the fact that it has been found that veronal poisoning may be cured by coriamyrtin, the active principle of the European *Coriaria myrtifolia*, which is closely allied to tutin.

Pukateine, one of the alkaloids of the pukatea tree, has recently been studied (Fogg, *J. Pharm. Exp. Therapeutics*, June, 1935). Some of the experiments suggest that pukateine may be used as a narcotic without danger of producing the ill effects induced by morphia.

AMMONIUM THIOCYANATE AS A WEED-KILLER.—Ammonium persulphate, ammonium percarbonate and sodium perborate were found to have practically no toxic effect on ragwort. In experiments with ammonium thiocyanate and various chromate and bisulphite salts on bracken it was found that 2·5 to 5 per cent. solutions of these salts were capable of killing the weed. Ammonium thiocyanate in 5 to 10 per cent. solution was also found to destroy sorrel and Californian thistle.

Union of South Africa

Department of Agriculture and Forestry

SEASONAL VARIATIONS IN THE FREEZING-POINT OF SOUTH AFRICAN MILK*

IN a previous publication (Dept. of Agric. Union of S. Africa, *Sci. Bull. No.* 119) the freezing-point of milk from individual cows and of the mixed milk from various herds was shown to range from —0·528 to —0·561° C., with an average of —0·541. The following investigation was made to ascertain whether there is a definite seasonal variation in the freezing-point of South African milk.

Five herds from different parts of the Peninsula, comprising animals typical of those responsible for the milk supply of the town and suburbs, were selected for testing, in addition to the pedigree Friesland and Jersey herds of the Stellenbosch-Elsenburg School of Agriculture, situated about thirty-five miles from Capetown. Each herd was maintained at more or less the same strength throughout the year, and animals that had recently freshened were brought in to replace those that had been dried up. This meant that the composition of each herd from which samples were taken changed continuously throughout the year.

In every instance an aliquot portion of the well-mixed contents of each of the cans into which the milk had been filtered was taken, these portions were thoroughly mixed, and the sample for analysis was taken from them. With few exceptions all the samples were taken before the milk had been passed over the cooler. The Hortvet apparatus and technique were used throughout, and in every instance the milk tested was from the 10.30 a.m. milking, and the freezing-points were determined at fortnightly intervals throughout the year. The following table represents the results obtained with all the samples analysed. The total number of cows in five of the herds was 353, whilst the number of animals in the other two herds varied from time to time.

The lack of relation between the food supplied and the freezing-point of milk produced is well illustrated by the results obtained with a "Buckinghamshire" herd. This herd, which at first consisted of 80 cows but was gradually increased to 126, received the same rations daily from February to November, and yet the freezing-point of the milk showed fluctuations from month to month. With the Elsenburg herds, also, the freezing-points of the milks from two herds receiving

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* Chemistry Series, No. 144, Bull. No. 143. By L. Denis-Lester, M.Sc., Ph.D., A.I.C. Pp. 14. Printed in the Union of South Africa by the Government Printer, Pretoria. 1936. Price 3d.

Month	Freezing-point depressions		
1933	General average ° C.	Least ° C.	Greatest ° C.
February	0·542	0·535	0·549
March	0·540	0·535	0·550
April	0·539	0·528	0·548
May	0·540	0·530	0·550
June	0·541	0·530	0·548
July	0·540	0·530	0·546
August	0·543	0·530	0·533
September ..	0·540	0·533	0·551
October	0·545	0·536	0·556
November	0·544	0·540	0·555
December	0·545	0·540	0·551
1934			
January	0·545	0·540	0·555
Average ..	0·542	—	—

the same rations exhibited dissimilar variations. In every instance it was found that with no change in ration was it possible to effect a variation in the freezing-point of the milk. This, then, eliminates the type of rations supplied to the animals as a cause of the variations noted.

Graphs show that the freezing-point of milk is independent of the meteorological conditions to which the herd is subjected. The conditions of temperature and rainfall recorded for the twelve months were, generally speaking, perfectly normal. Two Elsenburg (School of Agriculture) herds, under identical conditions, showed dissimilar freezing-points, and the results obtained with the milk from the other herds indicate that identical freezing-points are encountered at widely different seasons of the year. The general average freezing-point of all the samples analysed in March, May, July, and September was identical.

It was established that the period of lactation and freezing-point of the milk are not correlated, that the points between which the freezing-point of milk varies do not show any material difference from month to month, and that the variations that occur are in no way connected with the food supplied and are independent of the season of the year.

INFLUENCE OF PERIOD OF LACTATION ON THE FREEZING-POINT OF SOUTH AFRICAN MILK*

A number of cows, 45 in all, that had recently freshened were selected from seven different herds. Approximately every fourteen days a sample was drawn from the well-mixed milk of each cow until the animal was dried up. The most convenient hour of milking was selected for each herd, and the samples were drawn from the same milking throughout.

The determinations were made as soon as possible after the sample had been taken, in order to avoid any complication due to increased acidity, and the Hortvet apparatus and technique were used in every instance.

The results are exemplified in a table of four sets, each set representing two members of the same herd. The food supplied and the meteorological conditions were constants for each set. The range of depression of the freezing-point of the milks of the four pairs was as follows:—I, 0·528° to 0·560° C., and 0·535° to

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* Chemistry Series, No. 144, Bull. No. 157. By L. Denis-Lester, M.Sc., Ph.D., A.I.C. Pp. 8. Printed in the Union of South Africa by the Government Printer, Pretoria, 1936. Price 3d.

0·556° C.; II, 0·528° to 0·560° C., and 0·528° to 0·556° C.; III, 0·534° to 0·552° C., and 0·529° to 0·549° C.; IV, 0·530° to 0·560° C., and 0·530° to 0·559° C.

Throughout the whole period of lactation the freezing-point of the milk obtained from each cow showed definite variations. As three pairs of cows calved on the same day it was possible to compare the depression of the freezing-point of milks from each pair at any stage of the lactation period.

Graphs representing the variation in the milks of one of these pairs show that on January 24th, 1933, three weeks after calving, the depressions of the freezing-point differed by 0·009° C. On April 25th, 1933, the difference was 0·020° C., and on November 3rd, 1933, both milks exhibited the same freezing-point. Further, it is evident from the graphs that a knowledge of the variations in the freezing-point of the milk from any cow would not make it possible to predict the variations in the freezing-point of the milk from any other member of this herd.

In order to compare the freezing-point depressions of milks from cows of different herds, a second graph was constructed. Here, again, the graphical representation of the results obtained shows that the variations can in no way be correlated with period of lactation; milks which at one stage exhibit very similar freezing-points, exhibit widely different freezing-points at another. Further, it is clearly shown that the variations, for the same interval of time, may take place in opposite directions.

It is therefore concluded that it is not possible to regard variations in the freezing-point of milk as being in any way due to the period of lactation of the animal from which the milk is obtained.

British Standards Institution

BRITISH STANDARD SPECIFICATION FOR CALIBRATED RECEIVERS FOR DEAN AND STARK APPARATUS

This Specification (No. 614—1936) is one of a series of B.S. Specifications for Scientific Glassware, the preparation of which was authorised by the Chemical Divisional Council.

The Dean and Stark apparatus is used for the determination of water in a variety of substances, such as, for example, petroleum and petroleum products, tars and tar distillates, paints, etc. This Specification is concerned solely with the graduated receiver of the apparatus. In the complete apparatus the side arm of the receiver communicates with a boiling vessel and the receiver is attached to a reflux condenser. The boiling vessels and condensers to be used are specified in the appropriate British Standard Specifications.

Copies of the Specification may be obtained from the British Standards Institution Publications Department, 28, Victoria Street, London, S.W.1. Price 2s. 2d. post free.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Examination of Meat for Freshness. A. Zwilling. (*Z. Unters. Lebensm.*, **1936, 72, 148–156.**)—The following chemical tests for freshness of meat recorded in the literature have been examined to ascertain how they compare with one another as criteria of the state of advanced or incipient decomposition of meat:—(1) Reaction to litmus and *p*H value; (2) ammonia-content by the magnesia method of Horowitz-Wlassova and by Nessler's reagent; (3) content of enzymes and bacteria by the methylene blue test, by the benzidine reaction, by the guaiacol reaction and by Tilmann's oxygen consumption method; (4) the presence of free organic substances by such reagents as silver nitrate, copper sulphate and acetic acid, (5) presence of sulphides by Badagjan's method (*cf.* ANALYST, **1932, 57, 720**), and these are compared with a bacteriological test and with such sensory tests as the colour, taste, smell and general appearance of the meat. For the magnesia test the meat extract is placed in a Petri dish with some recently ignited magnesium oxide, and the temperature of the dish is raised to 50° C. on a water-bath. Before the dish is warmed a strip of litmus paper moistened with a drop of carbon dioxide- and ammonia-free distilled water is attached to the inner surface of the cover; and a similar strip is attached to the outer surface to serve as a control. The reaction of the inner paper is noted in about five minutes. This test is recommended as a sensitive test for the initial stages of decomposition. The reaction of the extract with Nessler's reagent is a less sensitive test. The formation of turbidity and change of colour of the reagent indicate slight decomposition; if a precipitate forms, the decomposition is advanced. The magnesia test gives a positive result with an ammonia-content of not less than about 0·017 per cent. of ammonia, whilst the Nessler test gives a positive result if it is not less than about 0·025 per cent. The procedure for the bacteriological test is as follows:—The surface of the meat is singed by means of a red hot spatula, and a cut (5 to 6 cm. long by 4 cm. deep) is made by means of a sterile scalpel. A microscope slide is pressed against one side of the cleft and a second slide against the other side. The smears are fixed by the Gram method and stained with Löffler's methylene blue. The bacteria are counted in 20 fields. A few individual bacteria, varying in number from 2 or 3 to 20 or 25 per field, indicate stages between freshness and incipient decomposition. In perfectly fresh meat the *p*H value should not exceed 6·2, but the determination of the *p*H of the extract is not recommended as a reliable test. The benzidine reaction is a useful confirmatory test. The other tests mentioned are reliable only as indications of advanced decomposition. The meat investigated consisted of beef, mutton and pork, and the results were the same for each kind of meat. A. O. J.

New Rapid Method for the Determination of Egg in Pastry. G. Nadai. (*Z. Unters. Lebensm.*, **1936, 72,** 157–171.)—The reagents are a solution of ferric chloride containing 20 g. of the crystalline salt in 100 ml. and ammonium molybdate solution containing 30 g. of the salt per litre. The mixed reagent is prepared as required by adding 2 volumes of the ammonium molybdate solution to 5 volumes of the ferric chloride solution. The precipitated molybdic acid dissolves in the excess of iron solution. The finely powdered air-dried pastry is extracted with absolute alcohol, the proportions being 30 g. of pastry (which amount should not be exceeded) to 150 ml. of alcohol. After being heated for not more than 2½ hours the mixture is cooled to 20° C., and about 110 ml. are filtered. The alcoholic extract (100 ml.) is placed in a 200-ml. flask, and to it are added 50 ml. of pure acetone, 5 ml. of *N* hydrochloric acid and 15 ml. of the freshly-prepared mixed reagent. The hydrochloric acid and the mixed reagent should be measured accurately from pipettes. After standing for at least 2 or 3 hours the liquid is filtered through a tared filter-paper. The precipitate is transferred as completely as possible to the paper and allowed to drain well, after which, the flask and filter are washed with two 15-ml. portions of 80 per cent. (by vol.) acetone. The filter is then left overnight and finally dried for 30 minutes at 100° C. and weighed. A Gooch crucible may be used in place of the paper, but the paper is recommended as lending itself more readily to ignition as a subsequent check. The whole of the alcohol-soluble P_2O_5 is not precipitated as the complex compound, but only the egg phosphatide; cereal phosphatide is not included. Egg-free pastry and egg-white pastry gave the same P_2O_5 figure (about 0·005 per cent.). In this work pastry containing vegetable lecithin (*e.g.* soya lecithin) was not examined. By preliminary tests with pure egg lecithin it is shown that 80 per cent. of the phosphatide is precipitated as the complex compound. The precipitate contains MoO_3 12·38, P_2O_5 2·16, and Fe_2O_3 7·50 per cent. By multiplying by 5 the amount of P_2O_5 corresponding with the weight of precipitate found, the amount of lecithin P_2O_5 in 100 g. of the air-dry pastry is obtained. For rapid work a modification of this method is described, in which the precipitation takes place in conical centrifuge vessels terminating in narrow graduated tubes in which the volume of the precipitate can be read (*cf.* ANALYST, 1936, **61**, 770). A. O. J.

Iodine Value of Spirit Vinegars. A. V. Sassi, N. Florentino and J. C. Migliaro. (*Industria y Quimica*, 1936, **2**, 8.)—The substances present in spirit vinegar which are capable of absorbing iodine are ethyl alcohol, acetaldehyde, methyl acetol, aldol, protoplasmic remains of *Bacterium aceti*, and tannins derived from the wood shavings and the beech-wood casks in which the vinegar is manufactured and stored. The following method is given for determining the iodine value, which is defined as the volume in ml. of 0·01 *N* iodine solution absorbed by 25 ml. of the vinegar. Fifty ml. of 0·01 *N* iodine solution are added to 25 ml. of vinegar, and the mixture is treated with a conc. solution of potassium hydroxide until completely decolorised. After standing for 15 minutes the liquid is acidified with dilute hydrochloric acid (10 ml. of conc. acid made up to 100 ml. with distilled water), and the free iodine is titrated with a 0·01 *N* solution of sodium thiosulphate, a 1 per cent. starch paste being used as indicator. The iodine value is 50 minus the number of ml. of thiosulphate used. With spirit vinegars the addition of iodine and subsequent treatment with potassium hydroxide yields a slight whitish precipitate with an odour of iodoform; this does not occur with solutions of commercial acetic acid, the iodine value of which is practically zero. Iodine values up to 2·6 have been obtained with less pure acids. The iodine values of 46 samples of spirit vinegars, classified in ten groups according to the factory from which they were obtained, were as follows: 22·5 to 31·6, 28 to 59, 28·5 to 39, 35·3 to 46, 24·4 to 36, 35 to 42, 38 to 43, 27 and 26·5, 38 and 39, and 34.

E. M. P.

Differentiation of Butters prepared from Pasteurised and Unpasteurised Cream. H. Patzsch. (*Z. Unters. Lebensm.*, 1936, **72**, 138–139.)—In the reaction described by Waters and Zürn (*Z. Unters. Lebensm.*, 1935, **70**, 353; Abst., ANALYST, 1936, **61**, 123) for the detection of peroxidase in butter a pronounced colour does not appear immediately in the aqueous layer. Bengen and Bohm (*Z. Unters. Lebensm.*, 1934, **67**, 382) have shown that the concentration of hydrogen peroxide is of importance. The course of the reaction is rendered more rapid if freshly diluted 0·3 per cent. hydrogen peroxide solution, as recommended by Rothenfusser, is substituted for the 3 per cent. solution. The observation of Waters and Zürn (*loc. cit.*), *viz.* that the peroxidase diminishes with the duration of storage is confirmed. The dithizone test of Eble (*Z. Unters. Lebensm.*, 1934, **68**, 307; Abst., ANALYST, 1934, **59**, 827) is likewise not definite. When no colour is formed in the benzidine reaction a beige to brown colour occurs in the dithizone reaction which, according to Eble, would be regarded as an indication of the presence of raw milk. Butter samples known to have been prepared from pasteurised cream gave yellow to beige tints. The procedure adopted was as follows:—Two to 3 g. of butter are placed in a stoppered cylinder and shaken with 5 ml. of acetone until solution is complete. One ml. of a 0·4 per cent. solution of dithizone in acetone is added and then, after shaking, 10 drops of 75 per cent. lactic acid, followed by a single drop of 1 per cent. hydrogen peroxide solution. The mixture is then vigorously shaken for 20 seconds and allowed to stand for 25 minutes. A blue-violet colour was observed only in very few instances; at the most, the colour was grey or strawberry-red. The opinion is expressed that other substances present in the butter react with dithizone. A. O. J.

The Benzidine-Peroxidase Reaction with Butter. Waters and Zürn. (*Z. Unters. Lebensm.*, 1936, **72**, 140–143.)—In an earlier paper (*Z. Unters. Lebensm.*, 1935, **70**, 353; Abst., ANALYST, 1936, **61**, 123) it was shown that the detection of peroxidase with benzidine for the differentiation of butter prepared from pasteurised and unpasteurised cream was sensitised by the addition of magnesium sulphate solution. Large amounts of common salt in butter from pasteurised cream also lead to positive results, but the amounts of salt occurring normally in salted butter do not influence the test. To determine the effect of varying amounts of salt, the salt was added to unsalted butter prepared from pasteurised cream and incorporated by mixing thoroughly in a mortar. The butter was then allowed to stand overnight. The solvents used were ether and petroleum spirit. Saturated magnesium sulphate solution and a 20 per cent. solution were used as sensitisers, the other reagents being alcoholic 4 per cent. benzidine solution and 3 per cent. hydrogen peroxide solution. With ether as solvent, no blue colour occurred in 30 minutes with concentrations of salt up to 4 per cent. With 5 per cent. of salt, no colour appeared when the magnesium sulphate solution was 20 per cent., but a blue colour formed with the saturated solution. It was also observed that with butter containing 4 per cent. of salt the reaction took place only in the neighbourhood of salt crystals, which appeared as blue points. With petroleum spirit as solvent no reaction occurred with 0·1 per cent. of salt in 30 minutes. With concentrations of 1 per cent. and over, the reaction occurred in times varying from 2 to 5 minutes. Petroleum spirit is therefore not a suitable solvent. After the butter had been stored in the dark, but unpacked, for 4 days the tests were repeated, with the same results. A. O. J.

New Zealand Fish Oils. I. The Composition of Eel Oil (*Anguilla Aucklandii*). F. B. Shorland and I. G. McIntosh. (*Biochem. J.*, 1936, **30**, 1775–1777.)—The body-fat from a specimen of New Zealand eel (*A. Aucklandii*) was found to resemble closely that of the typical fresh-water fish examined by Lovern (*Biochem. J.*, 1932, **26**, 1978). Oxidation with alkaline permanganate and bromination, respectively, have shown that the C_{18} unsaturated acids contain some stearidonic acid in addition to the oleic acid, but there was no evidence of the presence of either linolic or linolenic acid. Determination of the vitamin *A* content gave blue values ranging from 4·3 to 12·0. The livers yielded only 2 per cent. of oil, but this had a blue value of 1300. S. G. S.

Anti-oxidants and the Autoxidation of Fats. VII. Preliminary Classification of Inhibitors. H. S. Olcott and H. A. Mattill. (*J. Amer. Chem. Soc.*, 1936, **58**, 2204–2208.)—The oxygen absorption method for the study of auto-oxidation, previously used for lard, was not suitable for vegetable oils, and the most satisfactory method was to use the ethyl esters of the oils prepared by refluxing them with absolute methyl or ethyl alcohol containing dry hydrogen chloride. The inhibitors effective with animal oils are not the same as for vegetable oils; thus oxalic, malonic, maleic, citric, and other aliphatic dibasic acids (but not their salts or esters), phosphoric and sulphuric acids, cephalin, and some phenolic compounds, exert a remarkable protective effect against the oxidation of the crude esters of hydrogenated cotton-seed and other vegetable oils. Esterification is not responsible for this marked difference from lard, since crude methyl and ethyl lard esters responded to inhibitors in the same way as the original lard. Partial purification of the esters by fractional distillation *in vacuo* renders them only slightly subject to protection from the acids and cephalin, but they were then protected by hydroquinone and the inhibitols (*J. Amer. Chem. Soc.*, 1936, **58**, 1627).* A mixture of the acid inhibitors and inhibitol concentrates gives a much greater protection than either separately; this applies to lard, to purified fatty acids, and to esters, and has also been observed with certain mixtures of phenolic and acid type inhibitors. The inhibitors are tentatively classified into Group I, acid type inhibitors; Group II, inhibitols and hydroquinone (which is effective with vegetable oils but relatively ineffective with crude vegetable oil esters); Group III, other phenolic inhibitors, including gossypol, gallic acid, catechol, pyrogallol, α-naphthol, etc. D. G. H.

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* The name "inhibitol" has been given to certain unidentified constituents of the unsaponifiable matter of various vegetable oils which possess the property of delaying oxidative rancidity in certain fats.

Italian Control of Essential Oils [Prohibition of "Pipelene"]. (*Perf. and Ess. Oil Rec.*, 1936, 27, 396.)—No further dispositions with regard to the Italian citrus oils industry have so far been promulgated. The importation of "pipelene" into Italy has been prohibited by a Decree. Pipelene is an adulterant encountered from time to time on the Sicilian market. Ogston and Moore state that the various qualities are composed of limonene, dipentene, and variable proportions of pinene, with some aldehyde (probably citral) and terpineol. The following results were obtained with three samples of "pipelene":

	Pipelene "+28"	Pipelene "+58"	
		A	B
Non-volatile residue, per cent.	5·36	3·58	1·68
Aldehyde, per cent.	7·05	3·80	3·65
Optical rotation at 15·5° C.	29·25°	54·20°	54·15°
Sp.gr. at 15·5° C.	0·8655	0·8580	0·8570
Alcohol index (salicylic acid test)	—	—	1·32

Vacuum fractionation of sample B gave a residue having $[\alpha]^{15\cdot5}$, 1·05°, and sp.gr. 0·9292 and containing 42 per cent. of aldehydes. Pipelene absorbs oxygen rapidly and resinifies easily. D. G. H.

Determination of Essential Oil in Cloves, etc. L. W. Raymond. (*Perf. and Ess. Oil Rec.*, 1936, 27, 393.)—The apparatus described is for the determination of essential oils in cloves and other materials, such as nutmegs, mace, etc., by distillation with boiling water or low-pressure steam, with or without cohobation. Samples consisting of 500 g. of cloves were used (1000 g. for stems and 500 g. for leaves), and there was close agreement in the results obtained in different experiments, and also with the subsequently obtained factory yields. The apparatus consists of a copper still (1 gall.) with a ½-in. side-tube near the bottom. The cork in the neck carries a glass bend, ½ in. in diameter, the end projecting into the still being covered with copper gauze to prevent solid particles being blown over. The condenser must be capable of giving a cold distillate when the still contents are boiled rapidly. The condensate runs into a separator consisting of an upper glass tube, 8 in. in length and 1¼ in. internal diameter, with a side-tube tapering at the bottom and ground to fit the neck of a 100-ml. graduated cylinder. Cylinders and tubes are numbered in pairs. A cork fitting the top of the separator carries centrally a glass tube, ½ in. in diameter, reaching to within about 2 in. of the neck of the graduated cylinder, and the side-tube is connected with the side-tube of the still. About 1200 ml. of water are introduced into the still with the material, and, after the separator and cylinder have been charged with water, the still is heated, gently at first, and later as strongly as possible (a small pellet of soft paraffin dropped into the still will control frothing). The condensate drops into the inner tube of the separator, where the bulk of the oil separates and falls into the graduated cylinder, and the remaining milky fluid passes up the outer part of the separator and returns to the still. Distillation is continued until the distillate is quite clear (about 8–9 hours for cloves). The condenser is washed out into the separator, which is then disconnected, and any drops of oil adhering to the inner tube are freed with a rubber-tipped glass rod. The graduated cylinder is rotated and left for some hours, and the volume of oil is read. The oil, which is more or less clear, is syphoned off and filtered, and the apparent density is determined, thus giving the weight of the oil, from which percentage is calculated. The apparatus may be used for low-pressure steam distillation with cohobation by placing the material in a long glass cylinder (such as a lamp chimney) fitted above the still with a perforated copper sheet on 1-in. legs at the bottom, and connected by ¾-in. tubing with the still. Above the charge is a piece of copper gauze, and a wide glass tube leads to the condenser, the cylinder being lagged with asbestos cloth. If cohobation is not required a tube and funnel are connected with the side-tube of the still to allow of the addition of make-up water. For oils lighter than water a different separator is used, consisting of inlet and outlet tubes (¼ in.) joined in a wide (1 in.) separating tube, on the top of which is ground a 100-ml. graduated cylinder open at the top. The light oil rises into this cylinder, and the rest of the distillate with heavy oil, if any, passes through the outlet back into the still. D. G. H.

True and Poisonous Star Anise. M. Wagenaar. (*Pharm. Weekblad*, **1936, 73,** 1490–1502.)—True star anise (*Illicium verum*) is obtained principally from Cochin China, and has an aromatic odour similar to that of anethole, whilst the poisonous variety (*I. religiosum*) occurs in Japan, and has an odour resembling that of camphor. The following are the principal distinguishing tests, and these refer to *I. verum* and *I. religiosum*, respectively:—The astro-sclerotic layer at the top of the fruit-stem (columella) is irregular in structure and similar in shape to idioblasts in *I. verum*, but is rounded and has no special distinguishing features in *I. religiosum*. A magnification of 70×, and the use of polarised light aid the observation of these differences. Addition of strong hydrochloric acid and β-naphthol to the powdered drug produces a grass-green colour (due to a triphenylmethane dyestuff) in the stone-cells, the remainder of the structure (and especially the tissues) being blue, blue-green or blue-red; with *I. religiosum* the colours are brown-red and permanganate-violet, respectively. If this same reagent is applied to the whole seed, the respective reactions are green and brown. The layer of cells immediately adjacent to the stone-cells of the epidermis of the seed has thin, colourless, wavy papillary connections with intercellular cavities, whilst with *I. religiosum* the cells are more easily visible, being thicker, more circular and brown in colour, and they appear to be more densely packed. If this structure is stained with a warm 20 per cent. solution of ferric chloride, the details are more easily seen, owing to the formation of a dark iron-tannin compound, and a magnification of 150× may then be used; a 0·25 per cent. solution of methylene blue, malachite green or fuchsin will also serve as a stain. If a crystal of phloroglucinol or orcinol, suspended in sulphuric acid, is added to a filtered extract of the sample in alcohol or acetone, the respective colours are red, which increases in intensity, and weak yellow which subsequently fades. On slow evaporation of the extract on a watch-glass a thick fragrant oil which does not crystallise, and a crystalline solid having the odour of safrol or cardamoms are deposited, respectively. The microscopical differences referred to above are illustrated in the original. J. G.

Determination of Strychnine in Easton's Syrup. N. Evers and W. Smith. (*Quart. J. Pharm.*, 1936, 9, 397–400.)—The B.P. method for the determination of strychnine in Easton's Syrup is not satisfactory for old syrups, but the following modification gives good results with both old and new syrups:—The B.P. method is followed to the stage at which the impure alkaloid is obtained; this residue is dissolved in 10 ml. of *N* hydrochloric acid, and the solution is filtered through a 9-cm. filter-paper into a separator. The flask and paper are washed with three further quantities of 5 ml. of *N* hydrochloric acid and then with 25 ml. of a saturated solution of sodium chloride, and the extraction of the filtered liquid is repeated by shaking with 5 successive quantities of 25 ml. of chloroform. The B.P. process of separation is then continued, and the residue from evaporation of the chloroform is weighed; it should be almost white. E. B. D.

Isolation of Rutin from Tobacco. C. Neuberg and M. Kobel. (*Z. Unters. Lebensm.*, 1936, 72, 113–116.)—Rutin, which is a flavone-glucoside (*Naturw.*, 1935, 23, 800) plays an important part in the colour change accompanying the conversion of green tobacco into the brown finished product. The freshly gathered leaves contain considerable amounts of rutin which is partly retained in the quick drying process, but is reduced in amount in the slow drying and fermentation processes. Five kg. of ripe long-leaved pipe tobacco are ground and boiled with 7·5 litres of water for 30 minutes. The residue is filtered off, covered with 5 litres of boiling alcohol and allowed to stand overnight, and the alcoholic extract is concentrated to a syrup in an evaporator. From the aqueous extract, which is allowed to stand in ice for 3 days, a precipitate containing rutin separates. After another 3 days a further portion separates, and after several weeks yet another fraction. The filtrate from these fractions is then concentrated to about 2 litres, and from this a further deposit is obtained. The combined deposits, after impurities have been removed by extraction with ether, are re-crystallised twice from water, yielding, *e.g.* 8·7 g. of pure rutin. The syrupy alcohol extract is triturated repeatedly with water, whereby the soluble portion is separated from the less soluble rutin. The viscous residue is dissolved in ether, and both the ethereal and aqueous extracts are allowed to remain in ice for a long time for rutin-containing deposits to separate. After purification, the rutin is added to that already obtained. The total yield in one experiment was 11·7 g. from 5 kg. of leaves containing 16·4 per cent. of dry matter, *i.e.* 1·43 per cent. of the dry substance. The identity of the product was confirmed by ultimate analysis, by its optical rotation, by its reactions with lead acetate and ferric chloride, and by its hydrolysis into quercetin, glucose and rhamnose. Rutin was isolated from cigarette tobacco in a similar manner by boiling 12·5 kg. with two portions of 19 litres each of water for 30 minutes and 1 hour, respectively, and a further extraction with alcohol as previously described. The yield was 12·7 g. or 0·68 per cent. of the dry substance. By roof-drying 5 kg. of the long-leaved pipe tobacco in such a manner that its green colour was not destroyed the yield of rutin obtained was 5·9 g., as compared with 11·7 g. obtained from the fresh leaves. Commercial roof-dried and fermented tobaccos yielded no rutin. It is concluded that decomposition of rutin occurs during drying. A. O. J.

Occurrence of Sorbitol in Tobacco. C. Neuberg and M. Kobel. (*Z. Unters. Lebensm.*, 1936, 72, 116–121.)—To investigate the occurrence of sorbitol in tobacco 12·5 kg. of fresh ripe leaves of cigarette tobacco were boiled with two portions of 19 litres of water for 30 minutes and an hour, respectively. Crude rutin was separated by allowing the extract to remain in ice for long periods, as described in the previous abstract. The filtrate from the crude rutin was concentrated to 5 litres, and to it were added 5·2 litres of basic lead acetate solution (D.A.B., VI, 1926*). The filtrate from this precipitation was concentrated to 5 litres, treated with 100 ml. of lead acetate solution and filtered, and the filtrate was treated with hydrogen sulphide and, after removal of the lead sulphide, was concentrated to a syrup, which was dissolved in water, made up to 2 litres and treated with 4 litres of alcohol, yielding 34 g. of precipitate. The filtrate from this was concentrated, dissolved in 1 litre of water, and treated with 3 litres of alcohol. The precipitate in this instance weighed 45·8 g. The filtrate was concentrated, dissolved in water, made up to 4 litres, and fermented with brewers' yeast to remove fermentable sugars. Of this solution, 3600 ml. were treated with 550 ml. of lead acetate solution and filtered, and the filtrate was treated with 25 per cent. ammonia solution until no more precipitate was formed. The precipitate resulting from the lead acetate treatment and that from the ammonia treatment were suspended in water, and treated with hydrogen sulphide, the liquids were filtered, and the filtrates concentrated to syrup. The former yielded 15·4 g. and the latter 47·85 g. of syrup. A portion of this syrup (42·5 g. corresponding with 10 kg. of tobacco) was dissolved in water and made up to 500 ml. Of this solution, 450 ml. were fermented with 1 per cent. of brewers' yeast. For the isolation of sorbitol the method of von der Heide (*cf.* ANALYST, 1929, 54, 422) was found to be successful. The fermented solution (425 ml. corresponding with 8·5 kg. of fresh tobacco) was boiled with 15 g. of animal charcoal for 2 minutes and, after filtration and washing, the clear filtrate was made up to 650 ml. Portions of this (65 ml. in all) were concentrated to a syrup *in vacuo*, and shaken with 0·8 ml. of benzaldehyde and 2 ml. of 50 per cent. by vol. sulphuric acid. After a few minutes, a dense white crystalline mass was formed. This was allowed to stand on ice for 12 hours, filtered off and washed free from sulphuric acid. The final product was identified as a mixture of di- and tribenzal-sorbitol. The yield of benzal-sorbitol is not constant, but varies from 1·6 to 2·2 g. per g. of sorbitol. As an average figure, it may be taken that 1 g. of benzal-sorbitol corresponds with 0·53 g. of sorbitol. For the cigarette tobacco containing 15 per cent. of dry matter the sorbitol-content was about 0·4 per cent. of the dry matter. The sorbitol-content of pipe tobacco was determined by a similar process. This contained 16·4 per cent. of dry substance, and the sorbitol, expressed on the dry leaf, was 0·34 per cent. A. O. J.

Anomalous Viscosity of Tragacanth Mucilage. G. Middleton. (*Quart. J. Pharm.*, 1936, 9, 493–505.)—With the falling sphere viscometer, the time of fall of the first of a series of balls through tragacanth mucilage was abnormally high, even when the mucilage was tested only 2½ minutes after being vigorously shaken *in vacuo*. The anomalies are therefore not due to the reduction of viscosity on shaking with subsequent increase on standing, as in the isothermal reversible sol-gel transformation, known as thixotropy, which occurs with hydrophilic colloids of high viscosity, such as gelatin. Anomalies observed with tragacanth mucilage are ascribed to a new phenomenon, "stream orientation," caused by the orientation of long colloidal particles in the line of flow. The effect of accurately defined conditions of heating has been investigated. These conditions cannot be attained by immersing a flask in boiling water. Curves relating the dilution with the logarithms of the time of fall for different grades of gum form approximately a series of parallel straight lines. Results showing the effect of temperature on the apparent viscosity, expressed in seconds, are also given. E. B. D.

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* A mixture of 300 g. of neutral lead acetate, 100 g. of litharge and 1 litre of water is kept at room temperature for about a week, with occasional shaking, and then filtered.

Standardisation of Tragacanth. G. Middleton. (*Quart. J. Pharm.*, 1936, 9, 506–509.)—The definition of tragacanth in the British Pharmacopoeia excludes all but first-class samples of the whole gum, but is not applicable to powder, for which no definite characteristics are prescribed. A limit for the viscosity of the mucilage is therefore required, to ensure uniformity, and, as the viscosity is not a definite constant, it is not stated in poises but in seconds for a standard test. The test, which is based on the work described in another paper (see preceding abstract), enables samples of poor quality to be eliminated. The method is as follows:—Six g. of the gum are added to 444 g. of water in a bottle of about 1 litre capacity, and allowed to stand for 2 hours or until completely softened. The mixture is repeatedly drawn by suction through a strainer of metal gauze (approximately ⅜ in. diameter and with mesh of the size of the B.P. No. 25 standard sieve) until uniform. It is allowed to stand overnight, the temperature is adjusted to 20° C., and air bubbles are removed by evacuating air from the bottle, shaking it vigorously, and allowing it to stand for 5 minutes. Air is then re-admitted, and the viscometer tube of the falling sphere viscometer is filled with the mucilage, which is poured down the side of the tube, so that no air-bubbles are entrapped. The centralising tube is inserted axially, and the apparatus is adjusted to be exactly vertical. A steel ball, ⅛ in. in diameter and 0·129 to 0·130 g. in weight, is dropped down the centralising tube. After the ball has reached the lowest mark another ball is similarly dropped, and its fall between the highest and lowest marks on the tube is timed. This operation is repeated until two successive balls do not show more than 2 per cent. difference in their successive times of fall. The mean time of fall per 5 cm. is then calculated; it should be not less than 40 seconds. For whole gum the concentration employed for the limit test should be 1 + 89, for the time of 40 seconds. It is proposed that the relative strength of a sample of tragacanth should be defined as that dilution which will require 40 seconds under the above-described conditions. E. B. D.

Determination of Ferrous Iron in Saccharated Iron Carbonate by means of Ceric Sulphate. C. G. Lyons and F. N. Appleyard. (*Quart. J. Pharm.*, 1936, 9, 462–470.)—Ceric sulphate, being less coloured, is preferable to potassium dichromate for the titration of ferrous salts when an internal indicator is used. It does not react with many organic compounds in the cold, and the presence of rare earth metals other than cerium in the commercial ceric oxide or sulphate from which the solution used is prepared does not interfere with the reaction. The titration of ferrous iron with potassium dichromate gives inaccurate results in the analysis of saccharated iron carbonate, owing to the liquid glucose which is present; ceric sulphate does not react with glucose. *Method.*—One hundred g. of ceric oxide are treated, in a large evaporating basin with conc. sulphuric acid, which is added, a little at a time, until a thick paste is obtained. This is dried over a water-bath, the lumps being broken up as they form. The dried mass is dissolved in about 4 litres of distilled water, and the solution is filtered and standardised against ferrous ammonium sulphate. About 0·5 g. of the saccharated iron carbonate is dissolved by heating it with 20 ml. of 25 per cent. w/v sulphuric acid. After cooling, one drop of ferrous *ortho*phenanthroline sulphate solution is added as indicator, and the solution is titrated with standardised (approximately $N/10$) ceric sulphate solution until the orange colour just disappears. The method is convenient and the end-point is very sharp; other indicators were found to be less suitable than that recommended. Sulphuric acid is preferable to phosphoric acid as a solvent for the saccharated iron carbonate. E. B. D.

Measurement of the Proteolytic Activity of Pancreatic Preparations. N. Evers and W. Smith. (*Quart. J. Pharm.*, 1936, 9, 392–396.)—The method of the B.P., 1932, for the determination of the proteolytic power of pancreatin is lengthy, the end-point is not easy to observe, and the *p*H is not adjusted to a definite point before the addition of formaldehyde. A new and more accurate method has been devised, for which the following solutions are required:—(A) *Casein solution.*—Four g. of Hammarsten's casein are dissolved in 90 ml. of water containing 3 ml. of N sodium hydroxide solution, the *p*H is adjusted to 8·7, phenolphthalein being used as external indicator, and the solution is made up to 100 ml. (B) *Neutral standard.*—To 10 ml. of the B.P. phosphate buffer solution at *p*H 7·0, one drop of a 0·1 per cent. solution of neutral red in 50 per cent. alcohol is added. (C) *Alkaline standard.*—One drop of a 0·1 per cent. solution of neutral red in 50 per cent. alcohol and 3 drops of a 0·1 per cent. solution of phenolphthalein in 50 per cent. alcohol are added to 10 ml. of the B.P. boric acid—potassium chloride—sodium hydroxide buffer solution of *p*H 8·7. (D) *Enzyme solution.*—The required weight of the sample is triturated with a little chloroform water in a small mortar, washed into a 100-ml. graduated flask, and made up to the mark with chloroform water. If insoluble matter is present, the liquid should be used unfiltered, as a suspension. *Method.*—A mixture of 30 ml. of (A) with a definite volume of the enzyme solution is diluted with water to 100 ml. Fifty ml. are taken for a control test, and the remainder is heated rapidly to 55° C., kept at that temperature for 20 minutes, and cooled rapidly to room temperature. To this and to the control solution, 5 drops of neutral red solution and $N/10$ acid or alkali are added until each colour matches the neutral standard. For matching, 10 ml. each of the sample, control, and standard are compared in test-tubes. Fifteen drops of 0·1 per cent. phenolphthalein solution and 10 ml. of formaldehyde solution (B.P.) are added to both liquids, which are then titrated with $N/10$ alkali until they match the alkaline colour standard. From the difference, which is due to amino-acids formed, the volume of standard alkali for a definite weight (*e.g.* for 1 g.) of the enzyme preparation is calculated.

It is essential that the quantity of enzyme used should be such as to give a titration result varying within narrow limits; 4·3 and 4·7 ml. are suggested. Commercial samples of pancreatin were found to vary widely in proteolytic activity and in solubility, and the price was no criterion of the activity. E. B. D.

Biochemical

Chemical Aspects of Dermatitis. H. E. Cox. (*J. Soc. Chem. Ind.*, 1936, **55**, 775–781.)—In an attempt to ascertain the real causes of dermatitis the effects of different classes of substances on the skin are discussed and their modes of action are classified. It is suggested that dermatitis arises from specific reactions between the invading substance (which first must penetrate the epidermis) and some constituent of the blood or serum. Substances which commonly act as irritants are (1) reducing agents, (2) oxidising agents, (3) substances affecting the oxidation-reduction processes, (4) specific poisons. Sensitisation is discussed and notes are given of the particular dyes, intermediates, impurities, accelerators and other substances which cause dermatitis either to workers in the industries or to users or wearers of garments, soaps, perfumes, cosmetics, hair dyes, etc.

Colorimetric Method for the Estimation of Choline and Acetylcholine in Small Amounts. F. J. R. Beattie. (*Biochem. J.*, 1936, **30**, 1554–1559.)—This is a micro-colorimetric method, and it is claimed that by its use quantities of the order of 0·3 mg. of choline in a concentration of 0·003 per cent. can be estimated with an error of not more than 3 per cent To 1 ml. of the solution under examination (which should contain 0·2 to 2·0 mg. of choline or 0·3 to 3·0 mg. of acetylcholine) 1 ml. of a freshly-prepared saturated solution of ammonium reineckate* is added. A precipitate of choline or acetylcholine reineckate separates. The choline reineckate has a glistening appearance; its precipitation is complete in less than 10 minutes, and it can be quantitatively precipitated at temperatures up to 60° C. The acetylcholine reineckate separates more slowly as a dull pink powder and for complete precipitation requires a temperature not exceeding 5° C. To ensure that the precipitation is complete the container should be surrounded by ice for 20 minutes. The difficulty in determining the acetylcholine may be avoided by hydrolysing it with 1 per cent. caustic soda solution for a few minutes at room temperature, the solution being neutralised before the precipitation. After precipitation is complete the solution is filtered by suction through a small asbestos-packed crucible, and the precipitate is washed once with 2 ml. of ice-cold water and twice with 2 ml. of absolute alcohol, or until the alcohol is no longer pink. The receiving flask is emptied and a test-tube is placed inside the flask to receive the acetone solution. Before applying suction 1 ml. of acetone is poured on to the precipitate, which rapidly dissolves. The acetone solution is sucked into the receiving tube, and successive small amounts of acetone are added until all the precipitate is dissolved and washed through. The tube is removed from the filter-flask, and the contents are transferred to a graduated tube or small measuring cylinder which can be read to 0·05 ml. The receiving tube is rinsed with acetone, and the washings are added to the graduated tube. The volume of the acetone solution is carefully noted, and the colour is compared with that of a standard solution containing 0·78 mg. of choline reineckate per ml. or with a methyl red solution of the same colour. The standard corresponds with 0·26 mg. of choline chloride or 0·42 mg. of acetylcholine bromide per ml. When the total amount of choline is small (0·2 to 0·3 mg.) the total volume of the acetone should not exceed 1 to 2 ml. in order to have a colour comparable with the standard. The comparison of the colour in such a small volume can be carried out in a microcolorimeter. When, on the other hand, the total amount of choline is large (2 to 3 mg.) dilutions up to 10 ml. are required. Colorimetric comparisons should be carried out in daylight. The standard solution containing 78 mg. of choline reineckate in 100 ml. of acetone was found unsuitable as a permanent standard, owing to the evaporation of the acetone and the fading of the colour. The artificial standard of methyl red is prepared by dissolving 0·0134 g. of methyl red in 5 ml. of $N/5$ sodium hydroxide solution and diluting to 500 ml. with water. For use, 4 ml. of this solution are transferred to a flask, 10 ml. of $N/100$ sulphuric acid solution are added, and the volume is made up to 100 ml. The dilute solution will retain its colour for several days, and the stock solution indefinitely. Several different samples of methyl red gave the same colour. S. G. S.

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* Ammonium reineckate has the formula $NH_4[Cr(NH_3)_2(SCN)_4]$ and is obtainable commercially. The preparation of the acid was first described by Reinecke (*Annalen*, 1863, **126**, 113).

Determination of Albumin in Urine. C. A. Sagastume and R. A. C. Gherzi. (*Rev. Fac. Cienc. Quim.*, 1935, **10**, 7–10.)—In a previous paper (*id.*, 1934, **9**, 49) the authors described a new reagent for the detection of albumin in urine. The reagent has now been modified, without reducing its specificity or sensitivity, by diminishing the quantities of ammonium sulphate and of phenol, the new formula being ammonium sulphate, 50; sulphosalicylic acid, 10; phenol, 3; and water, 100 g. The mixture is boiled until the solids have dissolved, and the solution is cooled and filtered. This reagent, which the authors name reagent "S," is as specific and sensitive as trichloroacetic acid, and more so than nitric acid. It can be used for the quantitative determination of albumin by gravimetric or centrifugal methods. Parallel determinations were made by the centrifugal method with Aufrecht's reagent and with reagent "S," the liquid in each instance being centrifuged for two minutes at 1500 r.p.m. The results by the new method were often slightly lower than those by Aufrecht's method (*e.g.* 2·40 as compared with 2·80 per cent.). This is attributed to the greater specificity of reagent "S," and also to the more compact nature of the precipitate. E. M. P.

Observations on the Phosphotungstic Acid Method of Determining Ascorbic Acid in Urines with low Ascorbic Acid-content. G. Medes. (*Biochem. J.*, 1936, **30**, 1753–1755.)—In using the phospho-18-tungstic acid method for the determination of ascorbic acid in urine (Medes, *Biochem. J.*, 1935, **29**, 2251; Abst., ANALYST, 1936, **61**, 55) special precautions must be employed for urines with a very low ascorbic acid-content. When the urinary pigments interfere with the yellow colour produced in the test, the colour of the standard may be altered by the introduction of one of the indicators which are yellow in acid solution, such as bromophenol blue. If the colour is greenish-yellow, this method is not applicable, as a large amount of indicator is necessary, and this introduces a large error. Alternatives are the use of a colour filter (Monochromat Wratten No. 75) in the ocular of the colorimeter or the use of compensating cups, so that the standard solution is backed by urine diluted to the same extent as that in the test solution. The cloudiness which frequently develops in these urines may be removed by centrifuging. Readings in the colorimeter should be taken within 20 ± 5 minutes. In a series of tests on urines with a low ascorbic acid-content it was found that the colorimetric and titration methods are of about the same accuracy, and with urines of higher ascorbic acid-content the colorimetric method gives the more accurate results. S. G. S.

Variations in the Carotene and Vitamin *A* Values of the Milk-fat of Cattle of Typical English Breeds. A. E. Gillam, I. M. Heilbron, W. S. Ferguson and S. J. Watson. (*Biochem. J.*, **1936**, **30**, 1728–1734.)—The vitamin *A* and carotene-contents of the milk-fats from the milk of each of eight cows were determined spectrophotometrically at monthly intervals from the day of calving to the end of lactation. Four groups of two cows were used—Shorthorn, Ayrshire, Friesian and Guernsey, and all were treated alike, being stall-fed during the winter and pasture-fed during the spring and summer under typical English conditions of management. The results indicated that individual variations among cows of the same breed were large, but that, except for the abnormally high values of colostrum, the carotene and vitamin *A* values of the butters were more dependent on the diet than on the stage of lactation. The following table indicates the summary of the results; all values are in mg. per 100 g. of fat.

Breed		Gross average value	Winter average	Summer average	Minimum values	Maximum values	Vit. *A*/ carotene ratio
Shorthorn	Carotene	0·27	0·25	0·29	0·09	0·54	2·5:1
	Vit. *A*	0·68	0·58	0·84	0·36	1·24	
Ayrshire	Carotene	0·36	0·27	0·41	0·11	0·69	2·4:1
	Vit. *A*	0·85	0·66	1·18	0·30	1·42	
Friesian	Carotene	0·40	0·35	0·47	0·11	0·85	2·25:1
	Vit. *A*	0·90	0·61	1·21	0·52	1·50	
Guernsey	Carotene	0·92	0·73	1·14	0·42	1·97	0·80:1
	Vit. *A*	0·75	0·54	0·95	0·37	1·42	

Colostrum showed a carotene-content between 2·90 and 4·60 mg. per 100 g. of fat and a vitamin *A* content between 1·13 and 3·51 mg. per 100 g. of fat, which in some instances was ten times higher than that of the later milk. A comparison of the summations of carotene plus vitamin *A* placed the breeds in the following order for the vitamin *A* activity of the butters: Guernsey, Friesian, Ayrshire, Shorthorn, but the difference between the last three breeds is not very significant. S. G. S.

Spectrographic Studies on the Antimony Trichloride Reaction for Vitamin *A*. I. The Relation between Tintometer Readings and Spectral Absorption of the Blue Solution. O. Notevarp and H. W. Weedon. (*Biochem. J.*, **1936**, **30**, 1705–1718).—A study of the absorption spectra of the blue colours obtained with the antimony trichloride reaction has shown that, with oils and concentrates, Beer's law is followed far beyond the concentrations used in practice. When the amount of the oil solution exceeded 0·5 ml. a slight falling off was observed, which was due to the dilution of the reagent and not to chemical inhibition by the oil. The amount of the oil solution was varied between 0·05 and 0·4 ml. with safety. The well-known fact that the blue readings are not proportional to concentration has been confirmed spectrographically, but, as the solutions follow Beer's law, this is a purely physical phenomenon. The relations between E and the blue reading which were obtained were

Blue value $= 5{\cdot}5\ E^{0{\cdot}7}$ for oils, max. $603 m\mu$
Blue value $= 8{\cdot}5\ E^{0{\cdot}8}$ for concentrates, max. $618 m\mu$.

It has also been found that if a blue reading B is obtained with a concentration C, then a reading b will be obtained with a concentration c, where

$b = B\left(\frac{c}{C}\right)^x$ and that $x = 0{\cdot}7$ for oils and $0{\cdot}8$ for concentrates.

The blue value, as read in the tintometer, for a solution with a given absorption maximum was 40 to 60 per cent. higher where the band was at $618 m\mu$ than when it was at $603 m\mu$, and the conclusion is drawn that, even if the reaction were not inhibited by an oil, a concentrate should always give a blue value nearly twice that of the corresponding oil if they are measured at the same reading. S. G. S.

Chemical Determination of Aneurin (Vitamin B_1) by the Thiochrome Reaction. C. P. Jansen. (*Rec. Trav. Chim. Pays-Bas*, 1936, **55**, 1046–1052.)—The method is based on the observation by Barger (*Ber.*, 1935, **68**, 2257) that aneurin (Vitamin B_1) is oxidised to thiochrome by potassium ferricyanide in alkaline solution. The fluorescence due to the thiochrome was measured in the fluorometer described by Cohen (*Rec. Trav. Chim. Pays-Bas*, 1935, **54**, 133) in which a photoelectric cell was used and galvanometer readings were taken. For a solution of pure aneurin, 0·1 ml. (containing 1 to 20γ) was placed in a 25 ml.-glass-stoppered cylinder (rubber stoppers give rise to fluorescent substances), and to it was added a 0·1 per cent. solution of potassium ferricyanide. For 1γ of aneurin 0·01 to 0·1 ml. were required, for 10γ, 0·03 to 0·1 ml., and for 20γ, 0·1 to 0·2 ml. After mixing, 3 ml. of 10 per cent. sodium hydroxide solution were added and the solution was again mixed. After one or two minutes the solution was extracted with 13 ml. of *iso*-butyl alcohol. The two layers were separated by centrifuging and from the upper layer 10 ml. were pipetted into the vessel of the fluorometer and the reading was taken. For the international standard powder (adsorbate) a quantity of 10 to 50 mg. was weighed exactly and transferred to a 25 ml.-glass-stoppered cylinder and 3 ml. of the 10 per cent. sodium hydroxide solution were added, followed by the requisite amount of a 1 per cent. solution of potassium ferricyanide. If 10 mg. of powder were taken 0·05 to 0·1 ml. of the ferricyanide was needed; if 30 mg. were taken, 0·1 to 0·2 ml., and if 50 mg. were taken, 0·3 ml. was required. The powder was stirred with the solution for 5 to 10 minutes, after which the mixture was extracted with 13 ml. of *iso*-butyl alcohol. Separation was effected by centrifuging and 10 ml. of the upper layer were measured into the fluorometer vessel. The fluorometer was standardised in each series of determinations by the fluorescence of a solution of quinine in $N/10$ sulphuric acid (0·3 mg. to 100 ml.). Very good agreement was obtained between this method and the biological assay of the international standard. It was also found possible to use the method for the assay of a yeast extract. Ten ml. of a 25 per cent.

extract in water at *p*H 3 were treated with 20 ml. of methanol. The precipitate was removed by centrifuging and 1 ml. was mixed with 0·1 to 0·3 ml. of 1 per cent. ferricyanide, 1 ml. of methanol and 1 ml. of 30 per cent. sodium hydroxide solution. This mixture was then extracted with 13 ml. of *iso*-butyl alcohol as described above. Alternatively, the solution from the methanol precipitation was treated with fuller's earth (300 mg. per 15 ml.) and the technique described for the standard powder was used. S. G. S.

Influence of Cooking and Canning on the Vitamin B_1 and B_2 (G) Content of Lean Beef and Pork. F. W. Christensen, E. Latzke and T. H. Hopper. (*J. Agric. Res.*, 1936, **53**, 415–432.)—Dried lean pork and dried lean beef, both raw and cooked, have been examined for their content of vitamins B_1 and B_2. In the assay for vitamin B_1 the method of Chase and Sherman was used, and in the assay for vitamin B_2 that of Borquin and Sherman. It was found that dried raw lean pork contained 24 units of vitamin B_1 per gram, which was equivalent to 7 units per gram of fresh pork. Dried lean beef contained 2·5 units per gram or 0·6 units per gram of fresh beef. When the meat was cooked at a temperature not exceeding 90° C. the pork lost 12 per cent. of its activity, and the beef lost 20 per cent. When the cooking was performed in a steam autoclave or pressure cooker at 10 lbs. pressure for 70 minutes the pork lost about 20 per cent., whilst all the activity of the beef was destroyed. The vitamin B_2 content found was nearly the same for both sources of flesh and no loss occurred as a result of cooking or autoclaving. The values obtained were for beef: raw 4·9, cooked 4·4, and autoclaved 5·1 units per gram, and for pork: raw 6·9, cooked 6·5, and autoclaved 7·3 units per gram. S. G. S.

Bacteriological

Gum-like Masses produced by Fungi and their Utilisation. Anon. (*Chem.-Ztg.*, 1936, **60**, 956.)—In the search for new raw material for the production of plastic substances, attention has been turned to new sources. As early as 1913 Blucher and Drause used a by-product of yeast extract for the production of a hard rubber-like substance "Ernolith," this being obtained by the action of formaldehyde on yeast cell residues remaining on the filters in the manufacture of yeast extracts. Recently, Sanborn made noteworthy experiments on the possibilities of the industrial use of rubber-like substances produced by the lower types of fungi and recorded the yield obtained with "*Oidium gummi,*" grown on boiled mashed potatoes to which a variety of sugars and glycerin were added, the best yield being obtained with glucose and mannose. The membranes of various species of micro-organisms have for a long time been used in technical processes. From their fleshy tissues valuable films and membranes are produced. When the fungus is dried, powdered and treated with appropriate solutions a uniform rubber-like mass is formed. In Germany a product so formed is used as synthetic leather. Mould fungi are especially suitable for this purpose on account of their long mycelia. With *Oidium lactic*, when grown on 200 ml. of boiled potato mash with glycerin (proportions not specified), there is a yield of 80 to 100 g. in four weeks. Apart from the hard membranes, the gelatinous liquid cultures are also of value. Mixed with rubber suspensions, these provide coating, binding and, after suitable preparation, insulating material. The following species of organisms have been used:—*B. coli* (*Escherichia leporis*), *B. lactis aerogenes*, *Mesentericus vulgatus*, *Oidium lactis*, *Oidium pulmoneum*, *Monilia candida*, *Aspergillus fumigatus*, *Mucor racemosus*, and *Penicillium guttulosum*. D. R. W.

Toxicological

Industrial Poisoning [Manganese, Tungsten]. W. Brandt. (*Chem.-Ztg.*, 1936, **60**, 901–905.)—In a review of poisoning occurring in industry by various metallic compounds, the effects of manganese and tungsten are referred to. *Manganese.*—Poisoning may occur through inhaling vapours or dusts containing manganese. The following symptoms have been observed: Weakness, sleepiness, lack of facial control, slow speech or disinclination to speak at all, spasmodic muscular twitching of hands and legs, and difficulty in walking. A case is on record of workers being seriously affected by inhaling dust while engaged on unloading cargoes of manganese ore. *Tungsten.*—Whilst little is known of poisoning by tungsten in industry, the case has been described of a laboratory manager who probably inhaled tungstic oxide vapour while carrying out a considerable amount of melting of 18 per cent. tungsten steel in a crucible heated at about 2500° C. by means of a high-frequency furnace. Two days afterwards there appeared on the hands and feet small pimples or blisters which gradually spread and contained fluid having an objectionable odour. After a week, the man became weak and feverish, and suffered pains in the head and back. At the end of ten days his general condition was bad—high fever, recurrent periods of weakness and diarrhoea. From the twelfth day, however, improvement followed. S. G. C.

Organic

Oxidation of Organic Substances with Perchloric Acid. A. Vialard-Goudou. (*Compt. rend.*, 1936, **203**, 565–568.)—The substance was heated with an excess of perchloric acid (65 per cent.; sp.gr. 1·61) in a sealed tube within the temperature-range 135° to 220° C. Gas-carbon remained unattacked below 180° C. Above this temperature attack was slow, the products being carbon dioxide and hydrogen chloride; carbon monoxide and a chlorinated substance, both in small amounts, were detected as intermediate products. With oxalic acid, an equimolecular mixture of carbon dioxide and carbon monoxide was formed at the lower temperatures, but above 155° C. the reaction proceeded according to the equation

$$4H_2C_2O_4 + HClO_4 \rightarrow 8CO_2 + HCl + 4H_2O.$$

With saturated hydrocarbons, the susceptibility to attack, whilst slight, increases with the length of the chain. Methane begins to be attacked at 210° C., and ethane at 205° C., with the production of carbon dioxide. Heptane and "petroleum ether" are attacked at 205° C., and give some carbon monoxide in addition to carbon dioxide. Unsaturated hydrocarbons are attacked at lower temperatures, ethylene and benzene showing evidence of charring at 145° and 135° C., respectively. Methyl and ethyl alcohols and ethyl ether react readily to form the two oxides of carbon. Acetic acid is attacked less readily than the alcohols, carbon dioxide being the main product. In general, the oxidation of the organic substance takes place without the production of free oxygen. It is concluded that the mechanism is one of direct attack on the organic compound by perchloric acid, and that the oxidation is not attributable to the action of thermal decomposition products of perchloric acid.

S. G. C.

Determination of Isopropyl Alcohol. H. Kemal. (*Z. anal. Chem.*, 1936, **107**, 33–34.)—A measured volume of solution (*e.g.* 15 ml. of a solution of *iso*-propyl alcohol, containing 1 g. per litre) is treated with 0·4 g. of powdered potassium dichromate and 3 ml. of 4 per cent. sulphuric acid. The flask is shaken and left to itself for 24 hours, after which the solution is made alkaline with potassium hydroxide, diluted with water (100 ml.), and distilled. The distillate (60 ml.) is treated with 40 ml. of *N* potassium hydroxide and 25 ml. of 0·1 *N* iodine, and allowed to stand for 15 minutes. It is then acidified with hydrochloric acid (1:1), and the liberated iodine is titrated with 0·1 *N* thiosulphate solution. This represents the excess of iodine over that required for the formation of iodoform from the acetone produced by oxidation of the alcohol:

$$3KOI + CH_3COCH_3 = 3KOH + CH_3COCI_3.$$
$$CH_3COCI_3 + 3KOH = CHI_3 + CH_3COOK + 2KOH.$$

W. R. S.

Action of Alkalis on Mixtures of Aromatic Aldehydes. J. C. Bailar A. J. Barney and R. F. Miller. (*J. Amer. Chem. Soc.*, 1936, **58**, 2110–2111.)—If a mixture of benzaldehyde and *p*-dimethylaminobenzaldehyde is acted on by 50 per cent. potassium hydroxide solution, a Cannizzaro reaction is induced for the benzaldehyde only. A mixture of 5 g. of each aldehyde was shaken vigorously with 20 g. of the potassium hydroxide solution for 2 hours, allowed to stand for 24 hours, diluted with 300 ml. of water, and extracted with three 40-ml. portions of ether. The ethereal extract was shaken with a saturated solution of sodium bisulphite (which precipitated part of the dimethylaminobenzaldehyde as the bisulphite addition product), and distilled. The fraction boiling between 200° and 206° C. was taken as benzyl alcohol; the yield was 2·2 g. (88 per cent. of the theoretical). After re-crystallisation the m.p. of the product in test experiments was 73° C. The recovery of the substituted aldehyde from the bisulphite compound was almost quantitative. No *p*-dimethylaminobenzoic acid could be obtained, but there was an 84 per cent. yield of benzoic acid from the aqueous residue from the ethereal extraction. A mixture of *m*-nitrobenzaldehyde and benzaldehyde when treated with 14 per cent. potassium hydroxide solution gave nitrobenzoic acid and nitrobenzyl alcohol, the benzaldehyde being unattacked. Seven cases of crossed Cannizzaro reactions between aromatic aldehydes were studied; in each instance one of the aldehyde pairs was a halogen substitution compound, and invariably it was preferentially oxidised at the expense of the other aldehyde.

D. G. H.

Analysis of Sulphated Oils. Committee on Oils, Fats and Waxes, No. 10. D. Burton and G. F. Robertshaw. (*J. Int. Leather Trades Chem.*, **1936, 20,** 495–498.)—Although trial tests are necessary in order to judge the behaviour of sulphated oils, some chemical control is also required, and the usual method of determining water, ash and unsaponifiable matter, and calling the remainder saponifiable or "sulphonated" oil, is subject to serious error. There is no accurate known method for determining the water, and the xylene method is regarded as unsatisfactory, giving results which cannot be relied on within at least 0·5 per cent. Further, the figure for ash is low with oils containing ammonium salts, and, owing to the difficulty of completely saponifying some oils, inaccurate results for the unsaponifiable matter are liable to be obtained. The following method for ascertaining the amount of oily matter in a sulphated oil is being considered by the Deutsche Gesellschaft für Fettforschung:—Fifty ml. of carbon tetrachloride (to form a seal against the acid), 100 ml. of water and 50 ml. of hydrochloric acid of analytical quality are placed, in the order named, in a separating funnel, and, after the addition of 5 g. of the sulphated oil, the funnel is immediately shaken vigorously (40 double shakes), left for 30 minutes, and shaken again. After standing overnight the carbon tetrachloride layer is run off into a weighed flask, and the remaining portion of the layer is removed completely by means of two or three 5-ml. portions of carbon tetrachloride, which are poured down the sides of the funnel into the weighed flask. The carbon tetrachloride is evaporated, and the residue is dried at 100° C., cooled for 20 minutes and weighed, re-dried and re-weighed. A second and third extraction may be made by shaking out the acid solution with 20 ml. of carbon tetrachloride in each instance. No free sulphuric acid is extracted by the carbon tetrachloride, nor is any appreciable amount of organically combined sulphuric anhydride retained by the aqueous layer; in fact, the extraction of the sulphuric ester is complete. Various sulphated oils were extracted by this method, and closely concordant results were obtained by different analysts. The water may be estimated approximately by difference after determination of the ash. D. G. H.

Determination of Damage in Silk. S. R. Trotman. (*J. Soc. Chem. Ind.*, **1936, 55,** 325–327T.)—Damage in silk may be detected by measuring the viscosity of a 2·5 per cent. w/v solution of the sample in an aqueous solution of zinc chloride (sp.gr. 1·67), the viscosity of a solution of undamaged silk at 20° C. being approximately 3 to 3·1 compared with water. (ANALYST, 1935, **60,** 492.) The test has now been satisfactorily applied to dyed and undyed goods, and particularly to the detection of deterioration due to processing. The least concentrated solution of zinc chloride that completely dissolves the silk in 24 hours was found to be one of sp.gr. 1·67. Silks degummed in various ways had the following viscosities: (*a*) heated for 1 hour in a solution of olive oil soap (10 g. per litre) at 85° C., washed and dried, 3·10; (*b*) as above with addition of 1 per cent. of sodium carbonate on the weight of soap used, 2·00; (*c*) heated as above with 5 per cent. of monopol soap and 2 per cent. of sodium metasilicate, 2·95; (*d*) digested for 12 hours at 37° C. with a solution containing 0·1 per cent. of pancreatin and 0·1 per cent. of soap, followed by heating with water at 85° C. and washing, 2·52. No fall in viscosity was noted with degummed silks dyed with acid, basic or direct dyestuffs unless the temperature exceeded 85° C. Prolonged heating at 85° C., heating the bath to the boiling-point, or addition of sodium chloride or sodium sulphate to the dye-bath caused a distinct fall in viscosity. Samples of undyed and treated silk were exposed to the light of a Fadeometer lamp for 24 hours. The viscosity of the original degummed silk was 3·11, and after exposure the greatest fall was with silk wetted with 0·1 *N* sulphuric acid, which gave 1·40, or with ferrous chloride (1 g. per litre) 1·42, and the least fall was with silk wetted with 0·1 *N* sodium hydroxide solution. Such exposure to light alters some of the properties of the silk, increasing the rapidity with which water is taken up and the amount absorbed, and the action of light is progressive. Degummed silk exposed for 8 hours to ultra-violet light from a mercury lamp became yellowish-brown in colour and did not dissolve readily in the zinc solution, or in hydrochloric acid or Loewe's solution. Ultra-violet light differs from sunlight in its action, the tensile strength of the silk being much affected. The tensile strength of a sample of unexposed silk was 7·85 g., becoming 6·80 g. after exposure to ultra-violet light filtered through Wood's glass, and 3·83 g. after exposure to the unfiltered light. D. G. H.

Age and Chemical Composition of White Fir Wood. I. H. Isenberg. (*J. Amer. Chem. Soc.*, 1936, 58, 2231–2233.)—A section of wood, 7 in. thick and 17 in. in diameter, was sawn from the selected Californian white fir tree at a point 12 ft. above ground level where the age was 160 years. The cross-section was marked following the 15th, 40th, 85th, and 125th annual rings from the periphery, and these zones were chiselled to sticks approximately 0·2 × 0·2 × 3·5 in., dried at room temperature, and chopped in a Wiley mill until the sawdust passed a 60-mesh screen (that passing 80-mesh being discarded). The following data were obtained: ash, solubility in cold and hot water, ether, alcohol, benzene, 1 per cent. sodium hydroxide solution and acetic acid; methoxyl, nitrogen, pentosan, lignin, cellulose and pentosan in cellulose. The total sawdust contained 5·98 per cent. of mannan and yielded 0·86 per cent. of carbon dioxide in the uronic acid determination. The methoxyl-content of the lignin isolated from the total sawdust was 14·8 per cent. In many respects the composition of white fir wood resembled that of white spruce. Since in most determinations the values calculated for the total wood from the data of the individual age zones agreed with the values determined experimentally, values for the sapwood and heartwood were calculated to give figures comparable with those of other authors. The values obtained for the various determinations for sapwood (S) and for heartwood (H) were as follows:—Ash, (S), 0·38, (H), 0·63; solubility in cold water, (S), 0·53, (H), 1·99; hot water, (S), 1·41, (H), 2·61; ether, (S), 0·20, (H), 0·25; alcohol-benzene, (S), 0·94, (H), 1·67; 1 per cent. sodium hydroxide solution, (S), 10·45, (H), 11·46; acetic acid, (S), 1·70, (H), 1·31; content of methoxyl, (S), 4·53, (H), 4·78, per cent. on oven-dry weight; pentosan, (S), 8·56, (H), 9·42; nitrogen, (S), 0·06, (H), 0·06; lignin, (S), 27·34, (H), 27·50; cellulose, (S), 64·59, (H), 64·29. These results follow the lines of those obtained for other American conifers, except that the lignin behaves like that of white cedar, and is higher in the heartwood. D. G. H.

Analysis of Lac. M. F. Taradoire. (*Ann. Chim. anal.*, **1936, 18,** 285–288.)—Lac is a mixture of a resin and waxes containing mineral matter, organic vegetable and animal débris, moisture and rosin (colophony). The following analyses are carried out on the coarsely-ground sample after it has been stored for a few hours in a closed bottle in order to allow frictional electricity to dissipate. *Organic impurities.*—The sample (10 g.) is extracted first with 95 per cent. alcohol in a tared thimble in a Soxhlet apparatus until no more colour is removed, and then with boiling benzene (to remove "lacceryl lacceroate"). The residue, which should be free from resins and waxes, is dried at 100° C. and weighed, and the ash of the original sample (which is determined in the usual way) is deducted from the result in order to obtain the organic impurities. *Moisture.*—The sample is placed in a vacuum over sulphuric acid at 20° C., until there is no further loss in weight. This method takes 8 to 9 days, but it avoids the changes in composition which occur on drying by heat. *Rosin.*—The only method which gives satisfactory results is based on that described by Schulz and Landa (ANALYST, 1923, **48,** 87), in which mercuric acetate is reduced to the mercurous state by abietic acid. The sample (0·5 g.) is dissolved at 50° C. in 10 ml. of glacial acetic acid (which should be free from formic acid and saturated in the cold with mercurous acetate), and a freshly-prepared solution of 3 g. of mercuric oxide in 50 ml. of a saturated solution of mercurous acetate in acetic acid is then added. After 1 hour at 50° C. the mixture is left in the dark for 1 hour, and the mercurous acetate is collected on a filter and washed by suction with the solution of mercurous acetate in acetic acid. It is then treated on the filter with 20 ml. of 20 per cent. nitric acid, the residue being washed with 300 ml. of boiling water until the filtrate produces no precipitate with stannous chloride. The filtrate is boiled for 20 minutes with 20 ml. of sulphuric acid (66° Bé) and an excess of potassium permanganate crystals, the latter being subsequently reduced by addition of solid oxalic acid. Votocek's method may then be used for the determination of the mercurous salt formed, by adding in succession 50 ml. of a standard solution containing 13 g. per litre of sodium chloride, sufficient sodium nitroprusside to produce a weak yellow colour, and a sufficient vol. (*n* ml.) of an acid solution of mercuric nitrate containing 24·2 g. of mercuric oxide per litre to produce a permanent haze. This last solution should correspond, volume for volume, with the sodium chloride solution, 1 ml. of which is equivalent to 0·0131 g. of rosin; then the rosin-content is given by $200 \times 0{\cdot}0131\,(50-n)$, the error being normally not more than 10 per cent. *Acid value.*—As the filtration of lac solutions is slow and difficult, it is preferable to titrate directly a solution of 1 g. of the sample in 50 ml. of neutral 95 per cent. alcohol, with a 0·1 *N* solution of potassium hydroxide in alcohol, phenolphthalein or bromothymol blue being used as indicator; this method gives results approximately 14 per cent. higher than with the filtered solution. Although the acid value increases with the rosin-content, there is no relationship enabling either of these values to be deduced from the other. *Waxes.*—A solution prepared by shaking 10 g. of the sample and 2 g. of tartaric acid with 200 ml. of cold 95 per cent. alcohol is allowed to stand for 12 to 24 hours until the waxes have collected on the bottom of the flask; the slight acidity accelerates the deposition. The liquid is then filtered through a tared paper, the residue being washed with 95 per cent.

alcohol first by decantation, and then on the filter, until the filtrate is colourless and no longer produces a turbidity when diluted with water. To obtain the waxes the amounts of ash and of organic impurities are deducted from the weight of the residue after it has been dried, first in air and then over sulphuric acid, under reduced pressure. Analyses of 53 various types of lac in scale form suggest that a material of good quality should contain (in percentages):—Ash, less than 1; organic impurities, less than 2·5; moisture, less than 2; rosin, less than 3; waxes, more than 2. With some samples the analytical results indicated that the waxes had been replaced by rosin, 9 to 11 per cent. of which was present, and in this event it is desirable to test for ethyl alcohol, which is the solvent usually employed in this process (*vide supra*). The sample (10 g.) is therefore steam-distilled rapidly, and the iodoform test is applied to the first 10 ml. of distillate. Lacs which had been de-waxed by extraction with alcohol and the exceptional samples referred to above gave positive results, whilst normal lacs gave no reaction. J. G.

Inorganic

Separation of Bismuth from Cadmium. R. Strebinger and G. Ortner. (*Z. anal. Chem.*, 1936, **107**, 14–17.)—The precipitation of bismuth as oxyiodide (ANALYST, 1928, **53**, 237) was found to give a quantitative separation of bismuth from cadmium. For the recovery of cadmium as sulphide from the filtrate the iodide must first be destroyed, as it prevents the quantitative precipitation of the sulphide. The filtrate is therefore evaporated almost to dryness, and the iodine is volatilised by another evaporation with nitric acid. Instead of a sulphide precipitation, the evaporation residue may be dissolved in water, the solution treated with an excess of potassium cyanide, and the cadmium deposited electrolytically.
W. R. S.

Determination of Small Quantities of Arsenic in Tungstic Acid. T. Millner and F. Kúnos. (*Z. anal. Chem.*, 1936, **107**, 96–100.)—Tungstic acid (10 g.) is moistened with water and dissolved in 10 ml. of 40 per cent. sodium hydroxide solution. The liquid is treated with 10 ml. of phosphoric acid (sp.gr. 1·7) on the water-bath for an hour. After cooling, the solution is transferred with a minimum of water to a 500-ml. distilling flask connected with a spiral condenser and fitted with a ground-in thistle funnel provided with a tap. Eighty-four ml. of strong hydrochloric acid are diluted with 16 ml. of water, and 10 g. of cuprous chloride and 1 g. of potassium bromide are dissolved in 60 ml. of the diluted acid. This mixture is transferred to the flask with 20 ml. of the diluted acid, and the contents of the flask are well mixed and distilled until 80 to 90 ml. of distillate are obtained. The distillation is interrupted, the balance of the diluted acid is added, and the liquid is again distilled for a quarter of an hour. The arsenic in the distillate is titrated with iodine after addition of excess of bicarbonate. A blank assay should be made with the reagents. Proceeding in the manner described, the authors recovered up to 90 per cent. of the arsenic used. It was only by conducting the distillation in a vigorous nitrogen-hydrogen current (70 : 30), purified by being passed over copper heated to 500° C., and admitted through the thistle-funnel, that a quantitative recovery was achieved. W. R. S.

Determination of Non-Metallic Inclusions in Steel and Iron. E. W. Colbeck, S. W. Craven and W. Murray. (*J. Iron and Steel Inst.*, Preprint, pp. 22, September, 1936.)—The various methods proposed for determining the amount of non-metallic included matter in ferrous metals are reviewed. The complex nature and numerous possible combinations of oxides, sulphides, etc., and the variation in character of these inclusions in different steels, renders the determination very difficult. Methods depending on solution of the metal in acids are regarded as of little value. Tests on plain-carbon steels by the iodine-solution method (Rooney and Stapleton, *id.*, 1935 (1), 249) and by the chlorine method, in which the iron is removed by heating in chlorine gas (of which a detailed description is given), gave fair agreement in results for total oxide-content, but whilst the figures for Al_2O_3 were comparable, the values for SiO_2 were higher, and those for FeO and MnO were lower, by the chlorine method. Raising the temperature from 300° to 500° C. in the chlorine method caused a decrease in the recovery of oxide inclusions. This is due to the fact, which was ascertained, that whilst chlorine at 300° C. attacks Fe_2O_3 and Mn_3O_4 only slightly, the attack increases appreciably with rise in temperature to 500° C.; SiO_2 and Al_2O_3 remain unattacked by chlorine at temperatures up to 550° C. Alloy steels of the 14 per cent. Cr, the 18 per cent. Cr/8 per cent. Ni and the 6 per cent. Cr/0·3 per cent. Mo types have been examined by the chlorine method, but as a reaction-temperature of 500° to 550° C. was required, the results for inclusions may be low. In the iodine-solution method, MnS is only partially soluble, whilst Fe_3P is almost completely insoluble, and the oxide residues are therefore contaminated with these constituents. The iodine method is inapplicable to alloy steels, owing to the presence of insoluble carbides. The vacuum fusion method may give good values for the total oxygen-content of certain steels, but the ability of this procedure to throw light on the amount and state of combination of the individual oxides is doubtful. The determination of non-metallic inclusions in cast-iron presents considerable difficulties. S. G. C.

Detection of Potassium with Racemic Acid. L. Szebellédy and J. Jónás. (*Z. anal. Chem.*, 1936, **107**, 114–116.)—For the detection of potassium as potassium hydrogen tartrate, the optically inactive racemic acid is recommended instead of commercial *d*-tartaric acid because the familiar supersaturation effect is not observed with racemic acid. Hence the test is more reliable and expeditious, although there is no appreciable difference in the solubility of the precipitates obtained by the use of the two different forms of tartaric acid. W. R. S.

Determination of Sodium and Potassium in Insoluble Silicates. C. C. Miller and F. Traves. (*J. Chem. Soc.*, 1936, 1390–1394.)—An examination has been made of the method of determining sodium and potassium directly in the aqueous extract obtained from silicates decomposed according to the Lawrence Smith procedure, the sodium being weighed as sodium zinc uranyl acetate and the potassium being weighed as perchlorate. *Decomposition of Silicate.*—A 0·5-g. sample of the dried powdered silicate is decomposed by heating with 0·5 g. of ammonium chloride and 4 g. of calcium carbonate as described by Washington (*Chemical Analysis of Rocks*, 1930, p. 142). The filtered aqueous extract of the cold sintered mass is made slightly acid with hydrochloric acid and diluted to 250 ml. in a graduated flask. *Sodium.*—A 25- or 50-ml. portion of the solution is evaporated in a platinum dish to remove hydrochloric acid, transferred with the minimum amount of water into a small beaker, and evaporated to 1 ml. The sodium is determined by the zinc uranyl acetate method (Barber and Kolthoff, *J. Amer. Chem. Soc.*, 1928, **50**, 1625). Re-precipitation of the triple acetate precipitate is advised in order to free it from small amounts of calcium salts. A blank test should be made on the reagents. *Potassium.*—A 200-ml. portion of the solution is evaporated to dryness. The residue is dissolved in water and the potassium is precipitated as potassium sodium cobaltinitrite by Hamid's method (ANALYST, 1926, **51**, 450). The precipitate is filtered off, washed with a saturated aqueous solution of potassium sodium cobaltinitrite, and decomposed with perchloric acid, and the potassium is determined as perchlorate in the usual way. Two other methods for potassium were investigated, depending, respectively, on (*a*) separation of calcium chloride from the alkali chlorides by extraction with anhydrous *iso*-amyl alcohol and (*b*) separation of alkaline earth and sodium perchlorates from potassium perchlorate by extraction with anhydrous ethyl acetate-*n*-butyl alcohol mixture. Whilst the results furnished by all three methods were equally good, the cobaltinitrite precipitation method was considered preferable for convenience and speed. The methods for sodium and potassium were substantiated in tests on Bureau of Standards samples of silicates. S. G. C.

New Method for the Quantitative Separation of Lithium, with Reference to its Determination in Insoluble Silicates. C. C. Miller and F. Traves. (*J. Chem. Soc.*, 1936, 1395–1399.)—Conditions have been found for the quantitative precipitation of lithium as lithium zinc uranyl acetate, which can be determined gravimetrically. *Reagent.*—Zinc acetate trihydrate (125 g.) is dissolved in 600 ml. of glacial acetic acid diluted to 1000 ml. with water. The solution is saturated with uranyl acetate dihydrate. Rather more than enough lithium zinc uranyl acetate to saturate the solution is added, and the mixture is shaken briskly. Before use, the solution is stirred mechanically for half-an-hour, to avoid supersaturation, and filtered. The reagent should be stored in a dark coloured bottle, as it deteriorates in the light; it should not be kept longer than one month. *Determination.*—The solution, free from sodium, containing up to 10 mg. of lithium chloride, is evaporated to dryness in a 50-ml. beaker. Ten ml. of the filtered reagent are added to the dry residue, and the mixture is stirred mechanically for 15 minutes and allowed to settle for 15 minutes. The precipitate is filtered off on a sintered-glass filter (No. 10G 3), on which has been spread a thin layer of asbestos, and washed 5 times with 2 ml. of the reagent, then 5 times with 2-ml. portions of 95 per cent. ethyl alcohol saturated with the triple salt, and finally with a little dry ether. The precipitate is kept at 40° C. for 10 minutes, allowed to cool to room temperature in a desiccator over calcium chloride, and weighed. The precipitate has the composition $LiZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$. The temperature of the liquid during precipitation must be maintained approximately constant and be about the same as that of the reagent used. Results very close to the theoretical were obtained in test experiments with 0·6 to 10·0 mg. of lithium chloride. The completeness of the precipitation was shown from the fact that practically the same results were obtained on re-precipitation, which was carried out by dissolving the precipitate in 10 ml. of 0·1 *N* hydrochloric acid, evaporating the solution until a crust formed on it (if the mixture was taken to dryness, the final results were too high), and then proceeding with the precipitation as described above. The presence of a small amount of potassium was without effect. The presence of 1·2 g. of calcium chloride prevented complete precipitation, and 0·12 g. of this salt caused the precipitate to be contaminated, and a double precipitation was required.

Application to Silicate Analysis. Determination of Lithium in a Mixture of Calcium, Sodium, Lithium, and Potassium Chlorides.—A 0·5 g. sample of the silicate is decomposed as described in the authors' previous paper (*cf.* preceding abstract), and one-tenth of the filtered acidified extract is taken. From this point two alternative methods are available. (*a*) *Extraction of lithium chloride by iso-amyl alcohol.*—The solution is evaporated to dryness in a 30-ml. beaker, and the residue is re-evaporated with 1 ml. of *iso*-amyl alcohol to ensure complete dehydration; 2 ml. of the alcohol and a small drop of conc. hydrochloric acid are added, the mixture is heated to boiling, and the hard mass is broken up with a glass rod. After cooling, the liquid is drawn off by gentle suction through an immersion filter into another vessel, and the residue is washed with small portions of the alcohol. A second extraction of the residue is advised. The *iso*-amyl alcohol is removed from the combined extracts, and the lithium is precipitated as triple acetate as described above. A double precipitation is required, as the lithium is accompanied by a small amount of calcium. (*b*) *Extraction of lithium chloride by acetone.*—The solution of the mixed chlorides is evaporated to dryness, and the residue, after dehydrating by heating at 150° C., is cooled in a desiccator over phosphoric oxide; 5 ml. of anhydrous acetone and a small drop of conc. hydrochloric acid are added, the mixture is warmed to soften the solid material, and the vessel is transferred to the desiccator to cool (lithium chloride is more soluble in the cold solvent). The extract is filtered as in (*a*), and the residue is washed with small portions of acetone. A second extraction is advised. After removal of acetone from the combined extracts, the lithium is precipitated as triple acetate. As the amount of calcium chloride extracted by acetone is much less than by *iso*-amyl alcohol, one precipitation of the triple acetate is sufficient. *Determination of sodium in silicates containing lithium.*—Sodium may be determined by the triple acetate method (*cf.* preceding abstract) in the residue after removal of the lithium chloride. When acetone is used to extract lithium chloride, this residue contains the sodium chloride together with most of the calcium chloride, and two precipitations of sodium zinc uranyl acetate are required. In the *iso*-amyl alcohol method, the calcium is extracted together with the lithium, and a single precipitation of the residual sodium is all that is necessary. S. G. C.

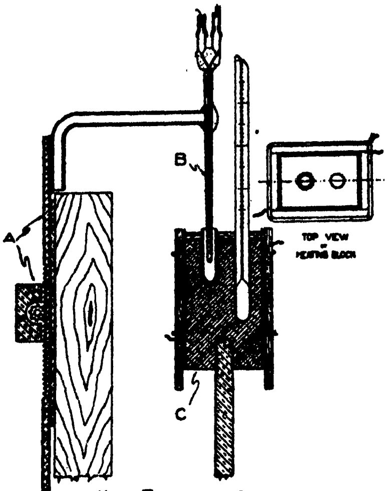
Co-precipitation of Ferric Sulphate with Barium Sulphate and Methods for Preventing it. A. Giacalone and F. Russo. (*Gazz. Chim. Ital.*, **1936**, **66**, 631–638.)—Barium sulphate was precipitated from 50 ml. of a solution containing 0·3664 g. of barium chloride dihydrate (corresponding with 0·3500 g. of barium sulphate) in the presence of 0·05 to 3 g. of ferric chloride, the liquid being acidified with hydrochloric acid to prevent the hydrolysis of the iron salt. Precipitation was effected at the boiling point, by means of 4 ml. of 20 per cent. sulphuric acid diluted to 15 ml. The precipitates, which were collected after heating for about 30 minutes and standing overnight, were faintly yellow to pink in colour. The results, which are tabulated, show that, in the presence of 0·05 to 1 g. of ferric chloride, the co-precipitation follows the equation $y = K.x^{\frac{1}{n}}$, where y is the weight in mg. of ferric oxide co-precipitated in 1 g. of the calcined mixed precipitate, x is the concentration of ferric chloride in the original solution in g. per 50 ml., and n is a constant, taken as 2; the results give 44·75 as the average value of K. At higher concentrations of ferric chloride the value of K diminishes. Further experiments showed that the weight of iron removed from the liquid was less than that weight, calculated as ferric oxide, adsorbed on the precipitate. Calcination of the precipitate does not convert into ferric oxide the ferric sulphate adsorbed in the particles of barium sulphate, but only that on the surface of the particles. The quantity of undecomposed ferric sulphate was determined. Re-calculation of K, expressing as ferric oxide all the iron co-precipitated with the barium sulphate, gave concordant values for K up to a concentration of ferric chloride of 4 per cent.; the average value of K was then 22·2.

The co-precipitation of iron with barium sulphate can be prevented if the ferric salt is reduced to the ferrous state before the precipitation. The most suitable reducing agent is ammonium thiocyanate, added in slight excess. The liquid is boiled until completely decolorised, and the barium is then determined as usual by precipitation with sulphuric acid. Concentrations of thiocyanate less than 1·5 per cent. (corresponding with 1 per cent. of ferric chloride) give pure precipitates; higher concentrations cause the decomposition of the thiocyanate, with deposition of sulphur. E. M. P.

Use of the Less Common Naphthols as Fluorescent Indicators. **M. Déribéré.** (*Ann. Chim. anal.*, 1936, **18**, 289–290.)—Five drops of a concentrated solution of the indicator in alcohol are added to 100 ml. of the liquid to be titrated (10 drops if the latter is coloured or turbid). On titration with sodium hydroxide the indicator changes from colourless and non-fluorescent to yellow, and, using derivatives of β-hydroxy naphthoic acid, the following fluorescence-colours are developed between the *p*H values indicated:—Anilide, bright yellow-green, *p*H 8·2–9·8; *m*-nitranilide, moderately-strong yellow-green, *p*H 8·5 to 10·2; α-naphthalide, bright yellow-green, *p*H 8·2 to 10·0; *o*-toluidide, intense yellow-green, *p*H 8·2 to 9·5; *o*-anisidide, intense yellow-green, *p*H 8·2 to 9·5; naphthazol-*NJ* (Kuhlmann) and 5-chloro-*o*-toluidide, bright yellow-green, *p*H 8·5 to 10·0; *p*-anisidide, bright yellow-green, *p*H 8·6 to 10·0; naphthazol-*NEL* (Kuhlmann) moderately strong yellow-green, *p*H 8·5 to 10·3; β-naphthalide, moderately strong yellow-green, *p*H 8·5 to 10·0. The end-points are sharper than that of β-naphthol, the fluorescence of which changes from bright violet-blue to a weak violet at *p*H 9·5, and the indicators are particularly useful for the titration of weak acids with sodium hydroxide in ultra-violet light, as they cover the usual phenolphthalein range (*cf.* ANALYST, 1936, **61**, 580, 640). J. G.

Microchemical

Fractional Distillation of Small Volumes of Liquids. A. A. Benedetti-Pichler and J. R. Rachele. (*Mikrochem.*, 1935–36, **19**, 1–5.)—The apparatus was devised for the separation of elements in a few c.mm. of liquid by distillation in inorganic qualitative analysis, with quantitative collection of the residue and nearly quantitative collection of the distillate. The cold-point condensation method is used. The apparatus is shown in the diagram, where A is a rack-and-pinion device for raising and lowering the condensing system B, to which attachment is made with De Khotinsky cement. The outer condenser tube, which is about 60 mm. in length, is drawn from 6 mm. soft glass and tapers from 1·5 mm. lower diameter to 3 mm. upper diameter. Inside the outer tube are two fine capillaries, each less than 0·5 mm. in external diameter. Both have an elongated bulb, 2 mm. in diameter, at the top for the attachment of rubber tubing. The shorter capillary is connected with a suction pump, and the rubber tube from the longer dips into a beaker filled with ice and water. In this way only the lower end of the condenser tube is cooled. The heating block, C, is made of aluminium, and its dimensions are 3 × 2 × 5 cm. It is covered with mica on four sides and wound round with about 2 ft. of No. 27 nichrome wire, for electrical heating, and insulated. The temperature is regulated by means of an external resistance (64 ohms) in series. The distilling tube is 2 to 3 c.m. long and is made from 6 mm. Pyrex tubing. *Application.*—Selenium was distilled as bromide from 1 c.mm. of 0·1 per cent. selenium solution (1γ of selenium) and 9 c.mm. of 9-molar hydrobromic acid. The distilling tube was centrifuged to bring the liquids to the bottom. Ice water was circulated, the distilling tube put in the heating block, and a very small drop of liquid bromine was placed on the tip of the condenser, which was then lowered into place. The distillation was carried out at about 90° C., and every 5 minutes the condenser tube was raised and the distillate removed with a capillary pipette, six fractions of 1·5 to 2 c.mm. being collected; the residue was free from selenium. The distillation was also complete with as much as 50γ selenium. J. W. M.



MICRO-DISTILLATION APPARATUS

FIG. 1.

Direct Micro-titration Method for Blood Sugar. B. F. Miller and D. D. van Slyke. (*J. Biol. Chem.*, 1936, **114**, 583–595.)—The method depends on the reduction of ferricyanide to ferrocyanide by the sugar, followed by a direct titration of the ferrocyanide with standard ceric sulphate solution in the presence of setopaline *C* as an oxidation-reduction indicator. The alkaline ferricyanide solution is prepared by dissolving 5 g. of potassium ferricyanide and 10·6 g. of anhydrous sodium carbonate in 1 litre of water. The ferricyanide should be recrystallised from water, and then rendered free from ferrocyanide by the method of Folin (*J. Biol. Chem.*, 1928, **77**, 421). This solution, when protected from light and dust, will keep for several months. A solution of sulphuric acid, approximately 18 *N*, is also required. This should be tested for reducing substances by adding 20 ml. of the acid to 60 ml. of water; after the addition of 0·05 ml. of 0·1 *N* potassium permanganate solution, the pink colour should persist for at least 5 minutes. The indicator solution is made by dissolving 100 mg. of setopaline *C* in 100 ml. of water. The stock solution of ceric sulphate is 0·1377 *N*, and is prepared by weighing 110 g. of anhydrous ceric sulphate into an 800-ml. beaker to which 35 ml. of concentrated sulphuric acid and 35 ml. of water are then added. The mixture is stirred and heated, and small amounts of water are added frequently until practically all of the ceric sulphate has dissolved. The solution is filtered, cooled and diluted to 1 litre. This solution may be standardised against a 0·1 *N* solution of ferrous ammonium sulphate by pipetting 15-ml. portions of the ceric sulphate solution into 50 ml. of water in a 150-ml. beaker, adding 3 ml. of 18 *N* sulphuric acid solution, and titrating with the ferrous ammonium sulphate solution until the colour of the ceric sulphate is almost bleached. Eight drops of the indicator solution are then added, and the titration is continued until the colour changes from golden brown to light yellow. The ceric sulphate solution is then adjusted to 0·1377 *N*. For the blood sugar titration a dilute solution of ceric sulphate is prepared by diluting 2 ml. of the stock solution with 5 ml. of 18 *N* sulphuric acid solution, followed by water to 100 ml. This solution has a strength of 0·002754 *N*, and 0·01 ml. is equal to 1 mg. of blood glucose when 0·1 ml. of blood is used for analysis. The solution loses its strength slowly and should be used fresh. An acid solution of cadmium sulphate is also required, and is prepared by dissolving 13 g. of cadmium sulphate ($3CdSO_4.8H_2O$) and 63·5 ml. of *N* sulphuric acid (free from reducing substances) in 1 litre of water. In addition, a 0·275 *N* solution of sodium hydroxide and a 0·275 *N* solution of sulphuric acid are necessary. If only blood sugar is to be determined, a micro-precipitation method is used for the removal of the blood proteins, but if urea is also to be determined a macro-precipitation method is preferred. In the micro-precipitation method 4 ml. of the acid cadmium sulphate solution are placed in a 15 × 150-mm. test-tube. Into this solution 0·1 ml. of blood is discharged from a pipette calibrated to contain this volume. The pipette is rinsed a few times by drawing the cadmium solution up into it. When the blood has laked to form a brown solution, 2 ml. of the 0·275 *N* sodium hydroxide solution are added and the tube is agitated until the contents are uniformly mixed. The tube is then heated in a boiling water-bath for 3 minutes and cooled in running water for 2 minutes. Approximately 0·3 g. of powdered barium carbonate is now added, and the tube is stoppered with the thumb and shaken for 10 to 12 seconds. The mixture is then filtered through a small plug of dry washed cotton-wool into a 50-ml. receiving test-tube, and the plug is washed with three portions of distilled water, each of 4 ml. The first portion of wash water is shaken a moment with the protein remaining in the precipitation test-tube; the other two are run down the inner walls of the tube. The filter should be allowed to drain almost completely before the next washing is added. If copper racks are used, a number of determinations may be carried out at the same time. If the macro-precipitation method is used, one part of oxalated blood is added to 8 parts of acid cadmium solution, followed by one part of 1·1 *N* sodium hydroxide solution. About 0·3 g. of barium carbonate is added for each ml. of blood, and the mixture is shaken for a few seconds. It is then centrifuged and filtered through a plug of dry washed cotton-wool. One ml. of this filtrate, equivalent to 0·1 ml. of blood is transferred to a 50-ml. tube and diluted with 14 ml. of water. Urea may be determined accurately in the cadmium filtrate, but creatinine values are 30 to 7 per cent. lower, and non-protein nitrogen 10 to 20 mg. per cent. lower than in tungstate filtrates. Two ml. of the alkaline ferricyanide reagent are added to the filtrate obtained by the above procedure, and the tube is gently whirled to mix the solutions. The mixture should be clear, indicating the complete removal of the cadmium. The tube is heated in a boiling water-bath for 15 minutes, then cooled in running water for 3 minutes. Just before each solution is titrated, which should be within 1 hour of reduction, 1 ml. of 18 *N* sulphuric acid is added, followed by 7 drops of the indicator. The titration should be carried out in a white light against a white background. The burette-reading, in ml., minus the blank, is multiplied by 100 to give the result directly in mg. of sugar per 100 ml. of blood. The blank determination is carried out by mixing 2 ml. of 0·275 *N* sodium hydroxide solution, 2 ml. of 0·275 *N* sulphuric acid solution, 14 ml. of water and 0·3 g. of barium carbonate, and shaking for 12 seconds. The suspension is centrifuged, and approximately 15 ml. of the supernatant fluid are poured through the cotton plug into the 50-ml. receiving tube. Two ml. of the alkaline ferricyanide solution are added, and the analysis is finished as described above. The cadmium sulphate is omitted because of the slowness of filtration, and the fact that it does not influence the blank. Whole blood may be preserved by adding 10 mg. of sodium fluoride per ml. Except in blood with marked nitrogen retention, the sugar found agreed closely with the fermentable sugar. The value found for venous blood was 83 mg. per 100 ml., with a standard deviation of 4 mg. and for capillary blood 92 mg. per 100 ml. with a standard deviation of 3 mg. S. G. S.

Microchemical Studies. XII. L. Rosenthaler. (*Mikrochem.*, 1935–36, 19, 17–22.)—(1) *Differentiation of yellow and red mercuric oxides.*—Red mercuric oxide reacts more slowly than the yellow oxide with a number of substances. The following reactions can be observed under the microscope:

	HgO (yellow)	HgO (red)
Ammonia	changes slowly to a white compound	remains red
Sodium bisulphite (conc. solution)	as with ammonia	remains red for a long time
Potassium bisulphate (10 per cent. solution)	in thin layers, rapidly turns bright yellow	remains red

(2) *Crystalline precipitations of vanillin.*—Baryta water causes vanillin to change into needle-shaped crystals; this reaction takes place with the drops of a micro-sublimate. Lime-water gives no reaction. Vanillin also reacts with lead acetate, giving rosettes of needle-shaped crystals. Further reactions below.

(3) *Differentiation between vanillin, ferulic acid, umbelliferone and methylumbelliferone.*—The following reactions are described:

Reagent	Vanillin	Ferulic acid	Umbelliferone	Methylumbelliferone
Sodium carbonate (saturated solution)	Bushes of long needles	At first solution then needles, etc.	At first solution, then slowly acicular crystals, some isolated, some in groups	——
Sodium hydroxide (50 per cent. aqueous solution)	Long needles on heating	Large, narrow or wide many-sided plates on heating	——	Yellow crystals, very slowly formed
Sodium hydroxide (saturated solution in methanol)	Needles	Needles formed more rapidly on heating	——	——
Zwikker's copper-pyridine reagent	Crystals of various colours and shapes produced over the drop	Fine brown needles, mainly in starlike groups, formed slowly	——	On heating, drops form, and, on standing, crystals
With acids from alkaline solution	Long narrow rods or needles	Groups of needles	Amorphous	Short prisms or long rods formed
Bromine and hydrogen bromide	Four-sided plates formed over the drops	——	Brown clusters over the drops	Clusters of fine brown needles quickly formed over the drop

(4) *Precipitation of phenols with p-diazo-nitraniline.*—The reagent consists of 2·5 g. of *p*-nitraniline, 25 ml. of water and 5 ml. of conc. sulphuric acid, the solution being diluted with 25 ml. of water and shaken, and a solution of 1·5 g. of sodium nitrite in 20 ml. of water added. After further shaking for a short time the solution is diluted to 250 ml. For the precipitation 5 ml. of the phenol solutions are used, and if they are dilute the result is observed after 24 hours. The following gave either amorphous or crystalline precipitates: phenol, *o*-, *m*- and *p*-cresols, vanillin, thymol, guaiacol, α- and β-naphthols, pyrocatechol, resorcinol, hydroquinone, orcinol, phloroglucinol, pyrogallol and apomorphine.

(5) Of the above-mentioned phenols, phloroglucinol and pyrocatechol react with Zwikker's copper-pyridine reagent,* to give deep blue and green crystals, respectively.

(6) *Crystal reactions of prontosil.*—Prontosil (I.G. Farbenindustrie) is the hydrochloride of 4-sulphonamide-2′,4′-diamino-azobenzene, and 0·2 per cent. aqueous solution of prontosil was used for the test, the solution containing starch and also talc. The following are the best reactions: with potassium cobaltidiammino-tetranitrate, with anthraquinone-monosulphonic acid, with silver nitrate, with mercurous nitrate and with copper acetate. There are 7 photomicrographs.

J. W. M.

Absorption Tubes for the Carbon-Hydrogen Determination. H. Friedrich. (*Mikrochem.*, 1935–36, **19**, 23–37.)—A new type of absorption tube with a single tap is shown in the diagram. It consists of two parts (*a* and *b*), which fit together (*c*). The groove in the ground tap-joint prevents the escape of any tap grease (3 parts of vaseline and 1 part of beeswax), and consequent loss of weight. Anhydrone is used for the absorption of water, of which the filled tube will absorb 80 mg. The carbon dioxide absorption tube is two-thirds filled with sodium asbestos (ascarite), and one-third with anhydrone; it will absorb up to 120 mg. of carbon dioxide with safety. A third (control) tube is used in conjunction with the two absorption tubes; this is filled with equal parts of anhydrone and sodium-asbestos. The tubes should not be weighed full of oxygen as the volume of gas inside is too large for the weight to be constant. The usual Pregl technique is followed, with electrical heating replacing the long burner. Freshly-filled absorption tubes are connected with the combustion tube, and oxygen is passed through for half-an-hour, followed by 100 ml. of air, and the control tube is then closed with a rubber stopper without disconnecting the apparatus, so that all the tubes are filled with air under slight pressure. The taps are turned, and the apparatus is placed on a stand by the balance case. After 5 minutes the taps are opened for 5 to 10 seconds to release the pressure and then closed again, and the tubes are wiped and weighed after standing for not less than 15 minutes. Any increase in weight in the control tube is subtracted from the weight of the absorption tubes, and any decrease is added. When possible, it is advisable to place the substance in the cool part of the combustion tube before weighing the absorption tubes, so that any impure air is blown out before the combustion begins. In determinations by the procedure described over a period of 8 months no results differed from the calculated values by more than 0·1 per cent. J. W. M.

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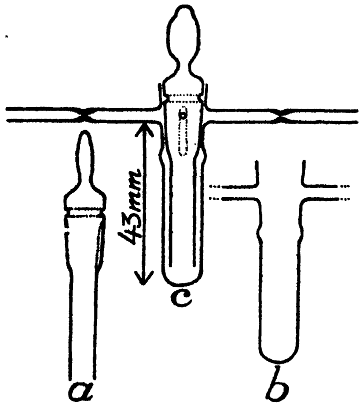
* A mixture of 4 ml. of 10 per cent. copper sulphate solution, 1 ml. of pyridine and 5 ml. of water.



Physical Methods, Apparatus, etc.

Determination by Ultra-violet Spectrography of Free Phenol and Sulphoconjugated Phenol in Pure Solution and in Blood. G. Barac. (*Bull. Soc. Chim. Belg.*, 1936, **45**, 641–646.)—The author has shown (*Rev. Belg. Sci. Médicales*, 1935, **7**, 669) that existing methods for the determination of phenols, such as the Folin-Denis reaction and the Marenzi diazotised *p*-nitraniline reagent, are insufficiently specific, and Lambrecht's method of spectroscopy in the ultra-violet has therefore been modified for the purpose. For the determination of ordinary free phenol, the solution in water is titrated iodimetrically in order to determine its approximate concentration, and a suitable volume is acidified with 20 drops of hydrochloric acid and extracted twice at room temperature with optically inert ether; the duration of each extraction is 3 minutes. The decanted extract is then diluted to a suitable volume with ether, dried, and examined in a large Jobin and Yvon quartz spectrograph, when 3 bands are visible with maxima at 267·0, 274·0 and 280·7$m\mu$, respectively; the molecular extinction coefficient for the band 280·7$m\mu$ is 2,400. The Beer–Lambert law applies to within 1 per cent., and the maximum recorded error with 0·00893 to 0·04465 per cent. of phenol is 0·00065 per cent. "Sulphoconjugated phenol" is the term given by the author to the product of the hydrolysis of potassium phenyl sulphate, and it is determined by hydrolysis of 50 ml. of the solution with 2 ml. of hydrochloric acid in a Pyrex tube (diam. 20 mm.) covered with a small funnel for 30 minutes in a water-bath at 100° C., the solution being extracted as described above when cool. The theoretical and experimental values with 0·01410 to 0·03800 per cent. of sulphoconjugated phenol were in exact agreement. Mixtures of the two types of phenol are evaluated by applying the above spectrographic method before and after hydrolysis, and determining the sulphoconjugated phenols by difference; slightly high values for the free phenol in such determinations may be due to hydrolysis of the compound phenol in the presence of acid at the ordinary temperature. These phenols in human, horse, cow or dog blood (whether arterial, venous, citrated, fresh or preserved on ice for some days) may be determined by the above methods, the Theis and Benedict tungstic acid reagent being first used to deproteinise the sample. The maximum recorded difference between the amounts added and found is 0·0042 per cent. J. G.

Spectrographic Analysis of Tin. D. M. Smith. (*Tech. Pub. Int. Tin Res. and Dev. Council,* Series A, No. 46, 1936, pp. 26.)—The use of both arc and spark methods has been investigated for the quantitative determination of impurities in tin, with special reference to aluminium, cadmium and zinc, over the range 0·001 to 1·0 per cent. The spark method was found to be the more sensitive in detecting traces of several elements, as shown by the following table:

LOWER LIMITS OF DETECTION

	Arc	Spark
Aluminium ..	Less than 0·001 per cent.	Less than 0·001 per cent.
Cadmium ..	„ „ 0·001 „	„ „ 0·001 „
Zinc	0·01 per cent. (approx.)	0·001 per cent. (approx.)
Antimony ..	0·03 „ „	0·03 „ „
Bismuth ..	0·001 „ „	0·0004 „ „
Copper ..	Less than 0·0005 per cent.	0·0005 „ „
Lead	0·0025 per cent. (approx.)	0·0025 „ „
Silver	Less than 0·001 per cent.	More sensitive than arc

Spark spectra photographed under standardised conditions of excitation, full working details for which are given in the report, are recommended for routine determination of aluminium, cadmium and zinc. A method has been worked out for the preparation of very pure tin by electrodeposition. S. G. C.

Reviews

RECENT ADVANCES IN PHYSICAL CHEMISTRY. By S. GLASSTONE, D.Sc., F.I.C. Third Edition. Pp. viii + 477. London: J. & A. Churchill, Ltd. 1936. Price 15s.

The change—in great measure a post-war change—which has come over the aspect of physical chemistry has made the science almost unrecognisable to those of us trained in the traditions of van't Hoff and of Ostwald. That stately progress through the realms of chemical statics and kinetics, ionic theory, the phase rule, thermochemistry—a progress illuminated, when need arose, by discreet applications of classical thermodynamics—all this is taken by the younger generation in its stride; and those tomes wherein the tale was told have almost all vanished from the scene, the ever-green and unapproachable Nernst excepted. But Nernst's great treatise is not for our generation only; it is indeed κτῆμα ἐς ἀεί, a treasure for all time.

It is no easy matter to provide those of us who would know something of these changes with an account of them which shall be simple, concise and reasonably accurate, and we cannot be too grateful to Dr. Glasstone, who has himself made important contributions to the science, for giving to us such an admirable summary of certain important topics. It would be difficult to overpraise Dr. Glasstone's work; the fact that within five years three editions of his book have been placed on the market speaks eloquently enough for the appreciation shown by the chemical world.

And the volume deserves the success which has fallen to its lot. The third edition of this work has sections dealing with Valency, the Parachor, Dipole Moments, Molecular Spectra, Homogeneous Gas Reactions, Photochemical Reactions, Surface Chemistry, Heterogeneous Catalysis, and Strong Electrolytes. The treatment throughout is quantitative, but not mathematical, the physical bases involved being rather explained and illustrated than developed *ab initio*. In the present volume the chapters have been revised and extended, and a section has been added which deals with the application of quantum mechanics to valency problems and molecular structure. ALLAN FERGUSON

RECENT ADVANCES IN GENERAL CHEMISTRY. By S. GLASSTONE, D.Sc., F.I.C. Pp. ix + 430. London: J. & A. Churchill, Ltd. 1936. Price 15s.

Dr. Glasstone's enthusiasm for explanation cannot be confined within the covers of a single volume, and his new book, which deals with advances in general chemistry, is concerned with Atomic Disintegration, Statistical Methods, Ortho- and Para-hydrogen, Deuterium and its Compounds, Electron Diffraction, Solubility, Reactions in Solution, Acid-base and Salt Catalysis and Simple Organic Free Radicals. Dr. Glasstone brings to these matters the same capacity for clear exposition which characterises his treatment of the topics elaborated in the parent book on Physical Chemistry (*supra*). And one welcomes the re-appearance, in extended form, of two of the chapters which exigencies of space had crowded out of the second edition of the Physical Chemistry.

It is usually courting failure to attempt an appeal to a wide and varied circle; but Dr. Glasstone's volumes can be confidently recommended to workers of an older generation who would keep in touch with some of these later developments which have transformed the science, to honours students seeking a preliminary mapping-out of fields of work to be later surveyed in detail, and to the post-graduate student embarking on research problems.

Carefully selected bibliographies are appended to each of the chapters, and add not a little to their value. ALLAN FERGUSON

A TEXT-BOOK OF ORGANIC CHEMISTRY. By the late Dr. JULIUS SCHMIDT. Third English Edition, by H. GORDON RULE. Pp. xxiv + 865. London: Gurney & Jackson. 1936. Price 25s. net.

The third English edition of Dr. Schmidt's well-known text-book of organic chemistry follows closely on the lines of the second English edition, an extensive review of which appeared in THE ANALYST (1932, **47**, 593). The text has been revised and brought up to date. New subject-matter includes an account of recent research work on the chemistry of the complex polysaccharides, the sterols and bile acids, the vitamins and hormones, and plant pigments. Reference is also made to new investigations in connection with the polymerisation of formaldehyde, the slow combustion of simple hydrocarbons, and carcinogenic compounds. The section on stereochemistry is particularly well written, and has been extended to include modern conceptions of the Beckmann Transformation, dipole moments in relation to molecular structure, and a study of the optically active derivatives of allene. The methods and results of these investigations are, in most cases, adequately described, and these additions enhance considerably the value and usefulness of the book. In several instances, however, the information given is much too scanty. For example, only two pages are devoted to the chemistry of the hormones. In a book of this type one would have expected to find the various stages in the synthesis of thyroxine clearly outlined and the formula of each intermediate compound graphically represented, as has been done in the case of several members of the group of alkaloids. This important substance, however, is dismissed in six lines, and even a very brief description of the method of synthesis is omitted. Insulin is not mentioned. Doubtless the necessity of keeping the size of the volume within reasonable limits is for ever before the author's mind; this new edition, in fact, contains only twenty-two pages more than its predecessor.

Taken as a whole, the book is without question the best of its kind in the English language, and the reviewer does not know of any other single text-book which contains a description of so many aspects of organic chemistry.

Although primarily intended for the use of honours students, for whom it is eminently suitable, the book is a valuable work of reference; the bibliography is extensive and mostly up-to-date. The book is written in an interesting and stimulating manner, and is remarkably clear and concise and free from errors. The numerous graphical formulae and tables are adequately represented. The indexes of authors and of subject-matter are very comprehensive and accurate. Dr. Rule is to be congratulated on the high standard which he has set and maintained. The work can be thoroughly recommended to both teachers and students of advanced organic chemistry. It is a most useful book to have at hand in the laboratory.

R. H. SLATER

MODERN VIEWS OF ATOMIC STRUCTURE. By K. RAST. Translated by W. O. KERMACK. Pp. 155. With 25 diagrams. London: Frederick Muller, Ltd. 1935. Price 7s. 6d. net.

This book gives an account, in non-mathematical language, of some of the work, theories and philosophy of modern physics in respect of the nature of matter, with special reference to the periodic classification of the elements.

Confidence in the reality of atoms has increased during the last quarter of a century, but in the same period it has been found that many elements, including hydrogen and oxygen, are not homogeneous, but consist of mixtures of two or more isotopes, whilst the elementary particles of matter are found to have some of the characters of waves. The Bohr–Rutherford theory of the atom has been developed in conjunction with the quantum theory and the periodic classification of the elements, and major features of the spectra of the elements have been interpreted in terms of atomic structure.

Dr. Karl Rast based two lectures on these themes in 1932 and 1933, and subsequently published them in German. The translator, Dr. W. O. Kermack, has added outlines of more recent advances, including the artificial production of radioactive isotopes of elements which has led to a Chemistry of Nuclear Reactions.

The author distinguishes between three planes of thought: the phenomenon itself, its description, and its explanation. He indicates that many explanations are really only descriptive, so that we are not very surprised "that Physics would not hesitate to acknowledge the same degree of truth in any other model (of the atom) if essentially the same mathematics applied to it—even though these two models should differ from one another as much as night from day . . ." It is regrettable that evidence of the wave nature of matter is omitted. Beams of electrons, protons, helium atoms, etc., can give diffraction patterns similar to those produced by rays of very short wave-length, and so there is nothing in the universe which is not at the same time possessed of both a wave nature and a corpuscular nature. This is true of quanta of radiant energy, which concept the author describes somewhat disjointedly. In contrast to this is his lucid description of the four quantum numbers which characterise an extra-nuclear electron in an atom. There are several minor inaccuracies in the text, and one has to read as far as p. 118 before discovering how pure a "pure" element (p. 23) is, whilst the title of a book by Jeans (p. 117), stated to be in the bibliography, has eluded discovery there. The German origin of the text is betrayed by the retention of J and Jn (p. 105) in place of I and In.

The volume is well produced, and those who have not been able to follow the rapid advances in atomic physics recorded in the literature will welcome it as a concise and readable account of the general position as late as 1935.

J. G. A. GRIFFITHS

THE CHEMISTRY OF THE COLLOIDAL STATE. By J. C. WARE, Sc.M., Ph.D. Second Edition. Pp. xvi + 334. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1936. Price 18s. 6d. net.

The first edition of this book was reviewed in THE ANALYST (1930, 55, 471). In the preface to the present edition it is stated that "The text has been largely re-written and, wherever possible, the practical applications of the colloidal state have been interwoven with the practical material. The space devoted to adsorption has been doubled, and the subject now occupies an entire chapter. A section on electrokinetic potential has been added to the chapter on the electrical character of interfacial phenomena. The chapter on the precipitation of colloids has been revised and extended to include the recently developed material on the subject. A new chapter has been included on intermediate cases and soaps."

The book is a curious blend of excellent accounts of certain phases of colloidal chemistry and some very elementary discussion. Thus, under emulsions: "Milk is a very stable emulsion and the fat globules are surrounded by thin elastic albuminous coverings. Cream is allowed to ripen so that a bacterial action weakens the covering of the fat globule. Then follows a churning process in which the films are broken and the fat globules released." The extensive investigations on the influence of the air/liquid interface on churning are quite ignored in this connection. In fact, the problem of foam in general is not dealt with in the text.

Again, although the preface states that a section on electrokinetic potential has been added to the chapter on the electrical character of interfacial phenomena, the subject is dismissed in twenty-one lines, and does not mention critical potential. More extended treatment should have been given to the important subject of the electrical double layer.

Although the whole treatment lacks balance, there are certain parts which will repay careful reading by students familiar with other elementary texts on colloids. Chapter II, on sedimentation, is noteworthy here. A useful feature is the inclusion of questions at the end of each chapter.

The reviewer believes that the book is suitable for those beginning to read colloid chemistry, if they are under the guidance of a teacher. A full subject-index is given, but there is no author-index. Students should begin early to check their knowledge by reference to the work of the leading investigators.

WILLIAM CLAYTON

ADDENDUM, 1936, TO THE BRITISH PHARMACOPOEIA, 1932. Pp. 132 and xx. London: Published for the General Medical Council by Constable & Co., Ltd. 1936. Price 5s.

Rapid and important progress in medical and pharmaceutical technique renders it necessary to make some recognition of the newest discoveries before the publication of a new edition of the British Pharmacopoeia, so that an Addendum has been published which became official on December 29th, 1936.

In former editions the changes and additions have been chiefly concerned with the pharmaceutical and manufacturing monographs, and additions and deletions which might have some effect on the work of the Public Analyst, but some of the newest items, now to become official, will be controlled by the Regulations of the Therapeutic Substances Act, 1925, rather than by the Food and Drugs Acts.

The 1932 B.P. included monographs on three antitoxins—Diphtheria, Tetanus, and Welchii, but the Addendum gives three more—Gas-gangrene, Staphylococcus, and Vibrioseptic—and provides methods for their biological assay and determination of potency with living animals. Two varieties of Antipneumococcic Sera are also to be official.

The technical details for testing such products are of the greatest importance, but the work can only be performed in specially equipped biological laboratories, which fact applies even more strictly to the testing of insulin, for which some important alterations have been included.

The important work of recent years on vitamins is recognised by the inclusion of Ascorbic Acid, Calciferol and Pulvis Vitamini B_1, and two new organic arsenical compounds are given official recognition—Acetarsol and Tryparsamide.

Histamine Acid Phosphate and Mersalyl are new to the official book, if not so new to medicine. Theophylline from natural plant sources, and Menthol from the Japanese peppermint plant, may now be replaced by synthetic preparations, but these must conform to very stringent tests for purity.

Ergometrine is the newest alkaloid introduced, and its two forms are differentiated. In connection with its tests, and also with those for ascorbic acid and calciferol, the optical rotation of solutions in anhydrous alcohol may be observed by either sodium light or mercury light; this optional method is a very useful one because of the increased illumination possible. The inclusion of ultra-violet absorption tests also introduces a new physical method for official work. The last monograph for Acriflavine is superseded by an entirely fresh one, and Calcium Gluconate is included for the first time. Chiniofon is a new iodine compound used in the treatment of amoebic dysentery and has been known for some while as a proprietary medicine.

Such important inclusions in the official book of reference make it an essential part of a modern analyst's equipment, but it may be a surprise, if not a grief, to find that the "blue values" of cod-liver oil are to be dispensed with, and tests for vitamins "*A*" and "*D*" by biological methods inserted.

"Redwood" viscosity is replaced by absolute viscosity, determined with standard viscometers, and the results reported in terms of *centistokes*, not *centipoises*.

Amendments concerned with numerous oils and volatile oils are of some importance to manufacturers and merchants, but the only new product introduced is Iodised Oil prepared by treating poppy-seed oil with hydriodic acid. The product is to contain 40 per cent. of combined iodine.

The compilation of the Addendum has been effected by the efforts of a number of sub-committees, and the changes made are evidence of the necessity for the Medical Council to keep the Pharmacopoeia Commission continually engaged in research and in the discussion of new products and improvements, as and when they are introduced.

C. EDWARD SAGE

FEBRUARY, 1937 Vol. 62, No. 731

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

SIR HERBERT JACKSON

SIR HERBERT JACKSON died, after a short illness, at Parsifal Road, Hampstead, on December 10th, 1936, in his 74th year. He was educated at King's College School, and in 1879 entered King's College, London, where he studied chemistry under Charles Loudon Bloxam, and later under John Millar Thomson, who succeeded Bloxam as Daniell Professor in 1887. After working for some years as Daniell Scholar and student-demonstrator with Bloxam, he was appointed lecturer and, in 1902, assistant professor. In 1905 he was appointed professor of organic chemistry and, in 1914, succeeded Thomson as Daniell Professor of Chemistry. In 1918 he retired with the title of Emeritus Professor, and accepted the appointment of Director of the British Scientific Instrument Research Association, which position he held until 1933. Subsequently he acted as consultant to the Association and served as a member of its Research Committee.

It will be seen that he was connected with King's College for nearly forty years, in the course of which many who later became members of this Society—including P. A. Ellis Richards, E. R. Bolton, Edward Hinks, F. W. F. Arnaud and John Evans (Past Presidents), and C. A. Mitchell (Editor of THE ANALYST)—came under his tuition. He took an active interest in all the affairs of the College, and participated in the annual sports, either as a competitor, starter or judge, or in some other official capacity.

He was an attractive lecturer, and although often discursive and unable to resist side issues, he could always pick up the thread again and hold his audience well with experimental demonstrations, which afforded him and them obvious satisfaction, and scarcely, if ever, failed. He was remarkably skilful in the handling of apparatus and instruments of all kinds, in glass-blowing and in the laboratory arts generally.

In 1883 he contributed to the Chemical Society a note on "The Action of Sulphuric Acid (sp.gr. 1·84) upon Potassium Iodide" and a note on "Bromine as a Test for Strychnine"; in 1884, a note on the "Action of Arsenious Anhydride on Glycerol."

A writer in *Nature*, January 2nd, 1937, recalls that before 1895

> "He carried out a lengthy investigation into the production of phosphorescent materials, and made an extensive study of the phosphorescent and fluorescent phenomena produced in various materials by ultra-violet light or by electric discharge in low-vacuum and high-vacuum discharge tubes. In the course of his experiments with high-vacuum tubes he observed that in some instances phosphorescent materials in close proximity to the tubes gave a luminous response when the tubes were excited. This observation was not followed up immediately, as it did not fall into the general line of investigation which was being pursued at the time, otherwise the discovery of *X*-rays, which was announced by Röntgen a few months later, might well have been made by (Sir) Herbert Jackson. Immediately Röntgen's discovery was published, (Sir) Herbert Jackson constructed an *X*-ray tube of the type described by Röntgen—the first *X*-ray tube to be produced in Great Britain—and thereafter he devoted a considerable amount of attention to a study of the effects which could be produced by the 'new' rays and to the development of *X*-ray tubes of improved forms. The 'Jackson' focus-tube, which he devised—and which he refused to patent—was a development of very great importance, since it provided practically a point source of *X*-rays and thus ensured sharp definition in *X*-ray photographs; the curved cathode which was its essential feature was adopted universally."

The use of the tube was demonstrated at a conversazione held at the Royal Society in May, 1896. On March 5th, 1896, however, he had read a paper before the Chemical Society in which he referred to the use of a cathode tube containing a concave aluminium cathode and a platinum anode inclined at an angle of 45°, *i.e.* the basic type of *X*-ray tube, unchanged in principle at the present day, which he first used as early as January, 1894 (*Proc. Chem. Soc.*, No. 162, 57–60). Röntgen made his announcement of the discovery of *X*-rays in December, 1895. Sir Herbert's work was on fluorescence and he had made his tube to deliver invisible radiation outside the tube, in order to study the effect of causation of phosphorescence in minerals and chemicals.

At another time he was interested in the protection of stone-work against weathering, and was consulted with regard to the restoration of Westminster Abbey and Canterbury Cathedral.

In 1898 he gave a discourse on phosphorescence before the British Association at Bristol (*Nature*, **58**), and in 1900 dealt with the same subject in a series of juvenile lectures at the Royal Society of Arts (1900, **48**).

In 1905, jointly with D. Northall-Laurie, he contributed to the Chemical Society a paper on "The Action of Carbon Monoxide on Ammonia," and in 1906, papers on "The Behaviour of Vapours of Methyl Alcohol and Acetaldehyde with Electric Discharges of High Frequency," and on "The Behaviour of Acetylene with Electrical Discharges of High Frequency."

In 1906 he gave a course of juvenile lectures on Combustion and Flame at the

Royal Society of Arts (**1906, 54**). About this time he turned his attention to the detergent properties of soaps and solvents and their effect on textiles, gave a series of lectures to launderers in London, to the substantial benefit of their industry, and a series of Cantor Lectures on Detergents and Bleaching Agents used in Laundry Work, before the Royal Society of Arts (1907, **55**).

In his investigation of glasses, for the Research Committee of the Institute of Chemistry and subsequently for the Ministry of Munitions, which he started shortly after the outbreak of war and continued until the armistice, he found his métier and his great opportunity. He was indefatigable and, in spite of difficulties arising from the shortage of supplies of certain essential materials, produced in a very little time—a few months—more than 70 formulae for batch mixtures for the manufacture of glasses and enamels, including optical glass, glass for miners' lamps, glasses for combustion tubing, capillary and thermometer tubing, laboratory apparatus, *X*-ray tubes, and ampoules, opal glass and enamels for artificial eyes, sealing-in enamels and vitrite for electric lamps, almost all of which had previously been imported from abroad. A glass similar to his miners' lamp glass was immediately adopted for cooking vessels which are now in general use. His early formulae were published in the Proceedings of the Institute of Chemistry, April, 1916.

Sir James Dobbie, then President of the Institute, gave him full credit for his remarkable achievements and, in March, 1916, the President of the Board of Trade expressed the Board's appreciation of the services rendered by Professor Jackson to the glass industry. In 1919 he delivered the Sir Henry Trueman Wood lecture at the Royal Society of Arts, on Glass and some of its Problems (1920, **68**).

He was elected a member of the Royal Institution in 1924, served as a Manager from 1930 to 1932 and 1934 to 1935. In March, 1927, he gave a discourse before the Institution on "Some Colouring Agents in Glasses and Glazes."

He demonstrated that it was possible to grow green plants in an atmosphere devoid of carbon dioxide, but containing from one to seventy per cent. of carbon monoxide. He also confirmed the formation of starch during such growth. Further work in this connection was carried out by Professor Bottomley and (Sir) Herbert Jackson at King's College, and the results were communicated to the Royal Society (**72**, 130).

He published very little else, but he did a great deal of work of which there is no permanent record.

If he did not achieve the reputation of a distinguished chemist so soon as he deserved, it was due to his dislike of putting pen to paper, although he was ever ready to impart his findings to his colleagues and students. Indeed, fellow chemists and others were often indebted to his inventive genius for original ideas, in the solution of problems and in devising chemical and physical apparatus, for which he received no material advantage and little or no credit.

Those who worked with him have remarked that, at times, he seemed to possess imagination or intuition which enabled him to foretell results with almost uncanny accuracy. Indeed, when a research worker suggested a problem he would very likely be informed by Professor Jackson that he himself had already worked on it and had obtained certain results. This was a little disconcerting, perhaps, and it was sometimes thought that he had deceived himself, or was merely surmising, but he was invariably right as to the results.

His other active work for the Institute of Chemistry, in addition to training many candidates for the Associateship, included an Examinership for the Intermediate Examination in general chemistry, which he held from 1908 to 1912, and in Mineral Chemistry for the final examination for the Fellowship, from 1911 to 1915. He was a Member of the Council from 1904 to 1907; a Vice-President from 1907 to 1908, 1916 to 1918, and 1921 to 1924; and a Censor from 1918 to 1935.

As President of the Institute (1918–1921) he was a good chairman, considerate to any opposition, clever in debate and definite in his decisions. Shortly after his election to that office, the Council revised the general policy of the Institute, so that he was called upon to guide its affairs during a period of unusual difficulty and responsibility, a period of reconstruction and resettlement following immediately on the termination of the war.

He was President of the Röntgen Society from 1901 to 1903, served on the Council of the Chemical Society, was a Vice-President and Member of Council of the Royal Society of Arts, an Honorary Fellow of the Royal Microscopical Society, Chairman or Member of several Committees connected with the Department of Scientific and Industrial Research and, for several years, a Member of the Senate of the University of London. He was elected a Fellow of King's College in 1907 and a Fellow of the Royal Society in 1917, and received the Honour of Knight Commander of the Most Excellent Order of the British Empire in the same year.

Of a happy disposition, versatile and entertaining, he will long be remembered by a host of old students and friends as a kind-hearted and public-spirited man.

He was elected a member of this Society in 1915.

RICHARD B. PILCHER

The Enzymes of Milk

I. Some Notes on Kay and Graham's Phosphatase Test*

BY E. B. ANDERSON, M.Sc., F.I.C., Z. HERSCHDÖRFER, PH.D., AND F. K. NEAVE, B.S.A.

(*Read at the Meeting, December* 2, 1936)

THE legal definition for pasteurisation of milk laid down for Great Britain has been reiterated in the new Milk (Special Designations) Order, 1936, which came into operation on 1st June, 1936. Apart from the Orla-Jensen Creamometric test,[1] which has certain limitations and which has never been adopted to any extent in this country, the controller of a pasteurising plant has possessed in the past no test of even approximate accuracy by which he could satisfy himself whether or not a sample of milk had been correctly treated. The need is clear therefore for a sensitive test to distinguish between milks heated correctly and those heated at a lower temperature than 145° F. or for a shorter time than 30 minutes.

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* This paper is a joint publication of work done partly in the laboratories of United Dairies, Limited, and partly at the National Institute for Research in Dairying. The work in the two laboratories was begun independently, that in the former laboratory being a section of a larger investigation of the enzymes of milk which is in progress under the joint direction of Dr. L. H. Lampitt and one of us (E. B. A.) and is being carried out in the Laboratories of J. Lyons & Company and of United Dairies; but after consultation with the Director of the National Institute for Research in Dairying it was agreed to avoid duplication of publication by combining the results in one paper.

Kay and Graham[2] have described a method based on the thermolability of the enzyme phosphatase in milk, which appears to meet all reasonable requirements for such a test. Their method has been recommended by the Ministry of Health[3] for use by local authorities. For details of the test reference should be made to the original paper.

We have subjected Kay and Graham's technique (their "Test B") to a careful examination, using the Zeiss–Pulfrich photometer for most of the colour determinations made.

REAGENTS AND APPARATUS.

STABILITY OF REAGENTS.—(i) *Buffer substrate.*—It has been found that if the buffer substrate solution of disodium phenyl phosphate and sodium veronal is kept in a refrigerator no hydrolysis appears to occur during at least 9 weeks. Even after 24 hours at 37° C., disodium phenyl phosphate does not show any evidence of hydrolysis at *p*H 9·8 (see Table I).

TABLE I

BUFFER CONTROLS TEST

Buffer sample	Extinction coefficient k	Lovibond blue units	Remarks
1	0·0806	0·3	Freshly prepared
,,	0·097	0·3	After 24 hours' incubation at 37° C.
2	0·075	0·3	Freshly prepared
,,	0·079	0·3	After 9 weeks in refrigerator

(ii) *Folin's phenol reagent.*—If correctly prepared the Folin reagent will be entirely free from any greenish tinge. We found it an advantage first to allow the bromine to act at room temperature for two hours and then to boil off the excess. The reagent did not show any sign of decomposition in four months.

The diluted Folin reagent (1 in 3) undergoes no change over a period of one week.

(iii) *Sodium carbonate solution.*—It has been found that, even when using AnalaR sodium carbonate, a precipitate formed in the solution after a short time.

As the intensity of the colour obtained by the test depends to a large extent on the concentration of this solution, it is advisable to control the strength by titration. It is also advisable to add a few drops of chloroform to the solution.

PRECAUTIONS AND SUGGESTIONS REGARDING APPARATUS.—(i) *Pipettes.*—Any errors in the measurement of the 0·5 ml. of milk will greatly affect the result; therefore only Grade A N.P.L. pipettes should be used.

A separate clean pipette must be used for each sample to be tested, as an admixture of as little as 0·1 per cent. of raw milk with a properly pasteurised milk may be sufficient to give a value above 2·3 Lovibond blue units. Accurate pipettes should also be used for delivering 2·0 ml. of sodium carbonate to each tube.

(ii) *Test tubes.*—Test tubes marked at 10 ml. should be used to receive the first filtrate, the maximum error tolerated being ± 0·1 ml. Tubes on the market often show more than this degree of error, and should therefore be tested before use.

(iii) *Filter-papers.*—Whatman No. 30 filter-papers have been used as recommended, but No. 42 (9 cm.) papers give more satisfactory results.

(iv) *Cleaning of glassware.*—All glass apparatus, including sample bottles, should be washed with hot soda solution and rinsed thoroughly with distilled water. The use of a phenol soap must be strictly avoided.

(v) *Apparatus for colour determination.*—Accurate readings may be obtained with a colorimeter or with a photometer. With the latter an accuracy of 0·02 unit is possible. Whilst such accuracy is not necessary in routine tests, it may be of value in precise investigations on phosphatase activity.

For making standard solutions for colour comparison in a colorimeter, etc., it has been recommended that dilute phenol and Folin's reagent should be used. We have found it equally satisfactory to use a solution of standard strength of a mixture of permanent dyestuffs. For this purpose, 0·10 g. of chlorazol brown L.F.S., 0·20 g. of chlorazol fast grey 2 G.S., and 0·30 g. of chlorazol steel blue 6 B.S. are dissolved together in 1 litre of water.* For use, 10 ml. of this stock solution are diluted with 28 ml. of distilled water; the liquid obtained gives 2·3 Lovibond blue units when tested in the tintometer in standard 13 mm. (rectangular) tubes.

Fig. 1 shows the relation between Lovibond blue units and the extinction coefficient with a selective red light filter, in the range of 750$m\mu$. The agreement is surprisingly good.

As is hinted above, the colour produced under the conditions of the test is not a true blue, but contains some red and yellow. It has been proved, however, that the amount of red and yellow is proportional to the amount of blue. The colour is stable for at least three days.

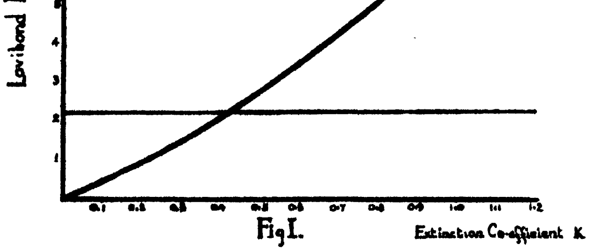

Fig I.

It should be mentioned that the colour is not specific for phenol, but is given by other substances such as ferrous iron and tin salts, tyrosine, etc. These substances, which should not be present in sufficient quantity in dairy products to be detectable by Kay and Graham's test, would in any case indicate their presence in the controls, and therefore would not be mistaken for enzyme-produced phenol.

SAMPLING OF MILK.—The usual care should be exercised in taking representative samples.

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* Our thanks are due to Imperial Chemical Industries, Limited, who kindly supplied suitable dyestuffs.

Milk samples taken from the refrigerator should be warmed to 15–20° C. before testing, and must be thoroughly shaken to ensure adequate mixing of the cream. This is particularly important when a cream plug has formed, as the major portion of the phosphatase appears to be associated with the fat-globules. The 0·5 ml. of milk used for the test should be taken from the lower half of the sample bottle and the pipette wiped clean before delivery of the contents.

EFFECT OF VARIATIONS IN TECHNIQUE.—(i) *Incubation.*—For incubation a water-jacketed incubator, or preferably a water-bath, either of which should be controlled at 37° C. ± 0·5° C., is essential. Table II shows the influence of different periods of incubation.

TABLE II

Ref. No.	Time of incubation Hours	Extinction coefficient k	Lovibond blue units
902	24	0·404	2·2
,,	26	0·425	2·3
904	24	0·490	2·7
,,	48	0·593	3·6
567	23	—	2·7
,,	24	—	2·7
,,	25	—	2·7

Variations of half an hour in the period of incubation do not seem to affect the result.

(ii) *Cooling.*—After incubation the tubes should be cooled below 20° C. Table III shows the effect, on the colour, of inadequate cooling before the Folin reagent is added.

TABLE III

Ref. No.	Temperature when the Folin reagent is added °C.	Extinction coefficient k	Lovibond blue units
903	5	0·418	2·2
,,	37	0·431	2·3
904*a*	5	0·490	2·7
,,	37	0·508	2·8
1104	20	0·360	1·9
,,	37	0·385	2·0

(iii) *Folin's reagent.*—In Table IV is shown the effect of varying the quantity of Folin's reagent added. It is evident that variations likely to occur have no effect.

(iv) *Filtration.*—Table V shows the effect of delay in filtration and emphasises the necessity of close adherence to the correct time, *viz.* 3 minutes, between adding the Folin's reagent and filtration.

A useful procedure is to collect the filtrates in test tubes marked at exactly 10 ml., and to remove the funnels as soon as 10 ml. of filtrate are obtained. This procedure, which avoids the necessity for using a separate 10-ml. pipette for each sample, has also the advantage of being an automatic time control.

TABLE IV

Folin's reagent	Lovibond blue units					
	Milk heated at 145° F. for 30 minutes			Milk heated at 142·5° F. for 30 minutes		
*2·0 ml.	2·1	2·2	2·2			
*2·5 ml.	1·7	2·0	2·0			
*3·0 ml.	1·9	2·0	2·0			
3·5 ml.	2·0	2·0	2·1			
4·0 ml.	2·0	2·1	2·1	5·0	5·0	5·0
4·5 ml.	2·0	2·1	2·1	5·0	5·0	5·1
5·0 ml.	2·1	2·1	2·2	5·0	5·0	5·0
5·5 ml.	2·2	2·3	2·3			

* Contains a high proportion of yellow, and blue colour has a tendency to settle out.

(v) *Addition of sodium carbonate.*—Fig. 2 shows the influence of different quantities of sodium carbonate added and demonstrates the necessity for precise measurement.

TABLE V

Ref. No.	Time of standing before filtration Minutes	Extinction coefficient k	Lovibond blue units
902	3	0·404	2·2
,,	15	0·478	2·7
904*b*	3	0·490	2·7
,,	15	0·504	2·9
1104*a*	3	0·360	1·9
,,	30	0·446	2·4

(vi) *Concentration.*—Fig. 3 shows the influence of changes in the concentration of sodium carbonate solution, 2 ml. of solution per test being used.

(vii) *Boiling.*—The effect of delayed boiling after addition of sodium carbonate solution is shown in Table VI.

TABLE VI

Treatment prior to boiling	Lovibond blue units				
	Sample 1			Sample 2	
Boiled immediately and without shaking	4·7	4·6	4·9	5·4	5·4
Mixed, then boiled after 1 min.	4·4	4·4	4·4	5·1	5·1
Mixed, then boiled after 5 mins.	4·3	4·3	4·3	5·0	5·0
Mixed, then boiled after 10 mins.	4·2	4·2	4·2	4·9	4·9
Mixed, then boiled after 30 mins.	4·1	4·1	4·1		
Mixed, then boiled after 40 mins.	4·2	4·2	4·2		

The effect of prolonged boiling on the development of blue colour is shown in Table VII.

TABLE VII

	Lovibond blue units				
Placed in boiling water for 5 minutes	4·2	4·2	4·3	4·3	
Boiled for 5 minutes	4·3	4·3	4·3	4·3	4·3
Boiled for 10 minutes	4·2	4·2	4·1	4·1	4·1
Boiled for 15 minutes	4·2	4·1	4·1	4·1	4·1
Boiled for 25 minutes	4·2	4·2	4·1	4·1	

The test should be made in duplicate and the results should agree within 0·1 Lovibond blue unit.

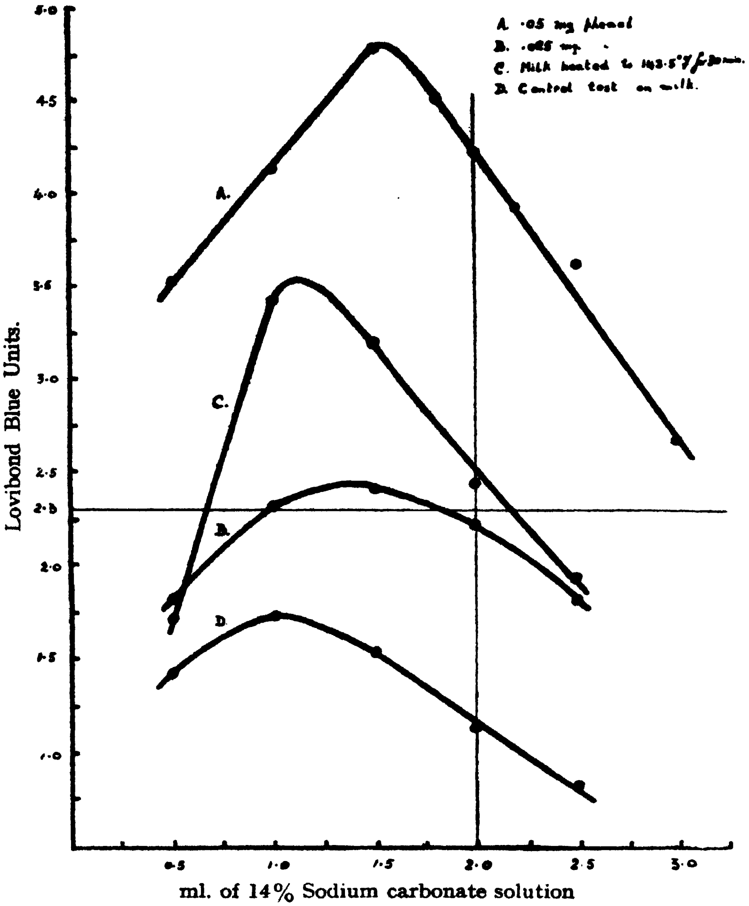

FIG. 2.

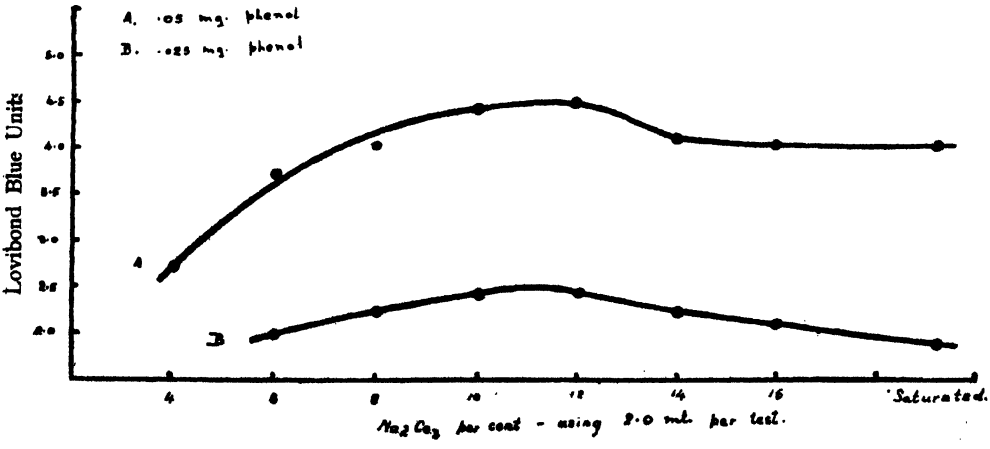

FIG. 3.

CONTROL TESTS.—The control tests, in which the activity of the phosphatase has been inhibited by the previous addition of the Folin's reagent, should be completed immediately. In the event of positive results, indicating the presence of phenol or other foreign substances, the contaminated samples may be eliminated at once.

The control tests must be made under the same conditions of temperature and time of standing as the main test, for Folin's reagent produces a slow hydrolysis of the substrate, as is shown in Table VIII.

TABLE VIII

10 ml. of buffer-substrate + 0·5 ml. water + 4·5 ml. Folin's reagent. Sodium carbonate added after keeping the test at different temperatures for different times

Time of keeping	Temperature of keeping	Extinction coefficient k	Lovibond blue units
3 minutes	5°	0·093	0·4
24 hours	5°	0·240	1·1
24 hours	37°	0·410	2·2

PRACTICAL APPLICATION.—*Effect of time and temperature of pasteurisation.*—A few figures may be of interest to illustrate the results obtained (see Table IX).

TABLE IX

Temperature	Lovibond blue units			
63° C. for 30 minutes	2·0	2·2		
62° C. for 30 minutes	2·8	2·7		
Time				
10 minutes at 63° C.	4.5	—	—	—
20 minutes at 63° C.	3·3	2·7	3·4	2·7
30 minutes at 63° C.	2·1	2·0	2·2	2·1
40 minutes at 63° C.	1·9	2·0	—	1·8

These figures illustrate how sensitive the test is to variations possible in actual pasteurisation.

TABLE X

INFLUENCE OF STORAGE OF PASTEURISED MILKS

Milk Sample No.	Time of storage	Temperature	k (S75)	Lovibond blue units
B	4 hours	Cold store	0·337	1·7
,,	7 days	,, ,,	0·307	1·6
,,	12 ,,	,, ,,	0·342	1·7
,,	15 ,,		0·334	1·7
D	0 hours	20	0·299	1·5
,,	24 ,,	20	0·314	1·6
,,	48 ,,	20	0·435	2·3
F	0 ,,	22	0·364	1·9
,,	24 ,,	22	0·378	2·0
,,	48 ,,	22	0·403	2·1
I	0 ,,	37	0·355	1·8
,,	20 ,,	37	0·547	3·8

Often it may be necessary to test a milk of unknown age. We have investigated whether prolonged storage affects the phosphatase-content of pasteurised milk. As shown in Table X, a milk sample kept at a low temperature will give the same result after a fortnight, whilst storage at a high temperature will give a higher reading according to the time and temperature. This increase in the colour may be due to the metabolic products of micro-organisms or to phosphatase of bacterial origin. Some knowledge of its history, therefore, is essential to an accurate judgment of a sample.

It has been found from the use of this test commercially over a period of 6 months that any interference by phosphatase of bacterial origin does not take place unless the milk samples have been kept under conditions which normally do not occur in this country.

Effect of admixture of raw milk.—According to our findings it is possible to detect an admixture of less than 0·25 per cent. of raw milk with legally pasteurised milk, as indicated in the following table:

TABLE XI

Raw milk added Per Cent.	Sample 1		Sample 2	
	k	Lovibond blue units	k	Lovibond blue units
0·00	0·328	1·7	0·332	1·7
0·10	0·423	2·3	0·498	2·8
0·25	0·498	3·1	0·667	4·0
0·50	0·871	6·1	0·945	6·6

CONCLUSIONS.—The phosphatase test of Kay and Graham for assessing the efficiency of pasteurisation of milk has been subjected to a detailed examination. The extent to which variations in the technique influence the result has been determined. As a result we find that, if satisfactory results are to be obtained with regularity, the published technique must be followed closely. Its practical application has been illustrated by reference to commercial samples.

We wish to thank the Directors of the United Dairies for their permission to publish that part of the work carried out in their laboratories, and Professor H. D. Kay for his interest in this investigation.

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1. Orla-Jensen, *Le Lait*, 1929, IX, 622.
2. H. D. Kay and W. R. Graham, *J. Dairy Res.*, 1935, 6, 191; Abst., ANALYST, 1936, 61, 44.
3. Circular 1533 of the Ministry of Health (April, 1936).

DISCUSSION

Professor KAY said that he had little to add to what Mr. Anderson had said. When he heard some little time ago that Mr. Anderson had given the method a searching trial and was finding it of real value he was very glad. He thought he ought to emphasise, what indeed Mr. Anderson had already implied, that it was a delicate method of some precision and required competent laboratory handling to obtain results that could be relied upon.

One small point he felt he should mention—the quality of the filter-paper. It was advisable to use a No. 42 Whatman paper. No. 30 could be used, but, on the whole, he preferred No. 42. Another essential was that the buffer substrate solution should be kept saturated with chloroform. He also pointed out that, whereas the test was very satisfactory for pasteurised mixed milks (taking the standard for failure as anything above 2·3 Lovibond units), for the pasteurised milk of individual cows some caution was necessary. It was, of course, most unlikely that milk of individual cows would be separately pasteurised commercially, but he had come across one or two cases in which milk of individual cows, pasteurised at exactly 145° F. and for exactly 30 minutes in the laboratory, had given figures of 2·3 or 2·4. This had never occurred, however, with commercial samples and was probably an academic point only. The reason for it was that the phosphatase-content of raw milk in individual cows varied considerably from one cow to another. It varied in a fairly regular way with the period of lactation. In the first few days it might be very high, then it went down to a minimum and remained low for some weeks, then it rose very high again at the end of the lactation period. If one happened to get hold of milk from an individual cow at either end of the period of lactation, one might get figures of 2·3 units, even when it had been perfectly pasteurised.

Mr. R. C. FREDERICK said that, with a view to its employment for a particular purpose, he had made an extended investigation of the rapid form of the test, and had reached the conclusion that it was excellent. He found that so long as the conditions of storage were such that the milk remained palatable, so long at least was the test reliable. With regard to the minimum amount of unpasteurised milk that could be detected, he thought that this must depend upon the reaction for phosphatase given by the pasteurised milk with which it was admixed. It was most valuable that the authors should have made this critical survey of a test which would undoubtedly become standard.

Mr. R. W. SUTTON said that he was surprised to find in Table II that 0·25 per cent. of raw milk increased the blue units to about 6. Was this ordinary raw milk or was it a special one? Could the authors give any test for over-pasteurisation —at a temperature higher than that specified or for a longer time?

Dr. HERSCHDÖRFER replied that the raw milk added was the ordinary milk supplied to the United Dairies Laboratory and not a special one. Figures such as these were obtained on the addition of 0·5 per cent. of raw milk.

Mr. D. MOIR said that, in his experience, the average blue value of the controls when the phosphatase test was first started (early in the year) was running at about 1·5; since then it had increased in the summer months to about 1·7 to 1·8, and now it was usually as much as 2·0; 2·0 was very close to the limit of 2·3 suggested for genuinely pasteurised milks when submitted to the actual test. Had Mr. Anderson had any experience of milks which gave a control blue value of over 2·3? Mr. Moir said that he had recently examined a pasteurised milk having a control blue value of 2·6. To what was such a high blue value likely to be due? Was the phosphatase completely destroyed if the milk was accurately pasteurised or was the final blue value in the test due to phenolic compounds in the milk and to residual phosphatase? Professor Kay had mentioned single cow milks being high in phosphatase and giving value slightly above 2·3. Presumably in such cases a little phosphatase was left. It had been shown that if milk were heated for a time only slightly less than 30 minutes or at a temperature only slightly lower than 145° F., a blue value considerably higher than 2·3 was obtained. Mr. Moir thought that, in view of these facts, the margin between the figures of 2·3 for correctly pasteurised milks and the control which might be as much as 2·0 was rather small.

Dr. HERSCHDÖRFER, replying, said that, of course, the phosphatase-content of raw milk was not constant, but, as a rule, 0·1 per cent. of raw milk was enough to give the test. If the raw milk was of very low phosphatase-content, however, it would require a higher percentage, but he had never had to add more than 0·2 per cent. As regards storage, when milks had been kept at a temperature not over 22° C., the kind of bacterial flora that developed seemed to have no influence on the readings.

Mr. A. PARKES referred to an experience in connection with a so-called pasteurised milk which gave a colour midway between those of raw and pasteurised milk; on investigation it was found that the milk had been held at pasteurising temperature for 2½ hours owing to the fact that the men had gone to lunch while it was being pasteurised. Could any explanation be given why the samples did not react to the test? The control gave the same colour.

Professor KAY remarked that it was most fortunate that the thermostability of milk phosphatase was such that it was completely or nearly completely destroyed when the legal minimum for pasteurisation time and temperature had been exactly fulfilled. Actually, if one pasteurised very accurately indeed at 145° C. for exactly 30 minutes, their findings showed that 1 part in 3000 or 4000 of the original phosphatase was left. In practice, the difficulty was to work at 145° C. exactly. Generally it was a little higher, so that the phosphatase in commercial practice was completely destroyed.

Regarding the short test—this had been put forward as a method of sorting out grossly under-heated milk and it worked very well for that. That was all that they had claimed. As to the amount of raw milk which could be detected, they had claimed originally 0·25 per cent.—they had been on the safe side, as workers in Denmark had recently submitted the test to careful scrutiny, and said that between 0·1 and 0·2 per cent. could be detected. There was no real difficulty with regard to over-pasteurisation of milk in commercial practice, because if milk was over-pasteurised, it affected the cream-line.

With reference to the question of getting above 2·3 in control tubes, that might be due to two or three things. They might have had some trouble with the filter-papers and that was a point which should be looked into. Another possible cause was if carbolic soap had been used by workers for washing their hands—this should not be used. A further possibility was that insufficient chloroform was added to the buffer substrate, and then one might get very slight hydrolysis of the substrate, giving free phenol in the control tubes.

The Detection of Arachis Oil in Olive and Almond Oils

By NORMAN EVERS, B.Sc., F.I.C.

(*Read at the Meeting, December 2, 1936*)

THE British Pharmacopoeia method of detecting arachis oil in olive and almond oils depends on a sorting test and a confirmatory test. A positive result with the sorting test is not a certain indication of the presence of arachis oil; the separation of arachidic acid and the determination of its melting-point alone gives reliable evidence on this point.

OLIVE OIL.—The sorting test was originally proposed by Bellier,[1] and was subsequently modified by several workers, including Franz and Adler.[2] In 1912 I reported on an examination of this test,[3] which I found very satisfactory. Only one "neutralised" olive oil out of a number of oils tested gave a positive result.

Since that time the character of commercial olive oils has changed considerably, and a very large proportion of olive oils give a positive reaction. For the purposes of this paper 26 oils were selected as representative of the olive oils at present on the market. Of these oils, 13 were described as finest edible oils, 1 was a "refined" oil, 8 were of "pharmaceutical" quality, and 4 were "commercial" oils. The countries of origin, as far as they were known, included Spain, France, Italy, Greece, Syria, Tunis, and Turkey. Of these 26 oils, 16 gave a positive indication with the B.P. sorting test, but in only one of these was the presence of arachis oil confirmed.

The formation of precipitates by genuine olive oils in this test has been noted by Shelley[4] and by Droop Richmond and Powell,[5] among others. Powell proposed to remove the unsaponifiable matter and carry out the test on the fatty acids. This certainly diminishes the number of positive results, but makes the test considerably longer.

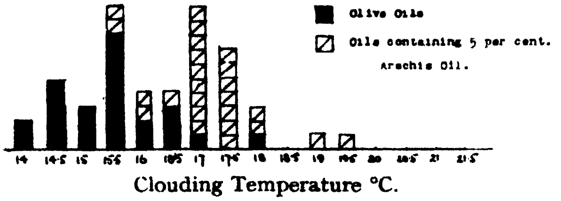
In the original test proposed by Bellier the oil was saponified with alcoholic potash, and acetic acid sufficient to neutralise the potash was added, followed by 50 ml. of 70 per cent. alcohol containing 1 per cent. of hydrochloric acid. The solution was then cooled to 17–19° C., and a precipitate showed the presence of 10 per cent. or more of arachis oil.

In the succeeding modifications the addition of hydrochloric acid to the 70 per cent. alcohol was omitted and only sufficient acetic acid was added to neutralise the potash used (or an amount slightly in excess of this). The resulting mixture gives a colour with methyl red corresponding to a *p*H of about 5·5 in aqueous solution, and the whole of the fatty acids are not set free. This is confirmed by the observation of Lüers[6] that olive oils giving a positive reaction contained an unusually high proportion of myristin, and that the precipitate consisted of the acid potassium salt of myristic acid. He suggested adding an additional 3 drops of glacial acetic acid to prevent this.

With a view to the elimination of some of the work which is now necessary to prove the absence of arachis oil from olive oils I have re-investigated the qualitative test. In the first experiments I reverted to Bellier's original test, in which 1 per cent. of hydrochloric acid was added to the 70 per cent. alcohol. This at once reduced the clouding temperature of olive oils, but it was found that a reduction also occurred when arachis oil was present. Further experiments showed that the addition of acetic acid was not essential, and that the results depended entirely on the *p*H of the solution. If, for example, the saponified liquid was brought to the same *p*H by adding hydrochloric acid instead of acetic acid, identical results were obtained. Tests were therefore carried out, omitting the acetic acid and adding sufficient hydrochloric acid to set free the whole of the fatty acids, the reaction being definitely acid to methyl red.

In Fig. 1 are set out the results obtained on the series of 25 genuine olive oils and on the same oils with the addition of 5 per cent. of arachis oil by this modified test and by the B.P. method. In the B.P. test the solution is cooled to 15·5° C., and if no turbidity occurs within five minutes at this temperature arachis oil is regarded as absent. It will be seen that 15 (60 per cent.) of the oils gave a turbidity at or above 15·5°C. Further, if the critical temperature is raised above 15·5° C., 5 per cent. of arachis oil cannot be detected with certainty.

B.P. TEST



MODIFIED TEST

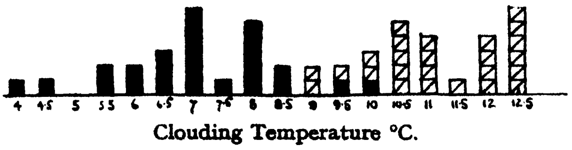


Fig. 1.

In the modified test all but two of the olive oils gave no precipitate above 8·5° C., and all the oils containing 5 per cent. of arachis oil were turbid at 9° C. If, therefore, the solution is cooled to 9° C., 5 per cent. of arachis oil will be detected with certainty, and only a small proportion of pure olive oils will become turbid at this temperature.

The modified test is carried out in the following way:—One ml. of the oil is saponified with 5 ml. of 1·5 *N*-alcoholic potassium hydroxide solution by heating on a water-bath for five minutes, avoiding loss of alcohol; 50 ml. of 70 per cent.

alcohol are added, followed by 0·8 ml. of hydrochloric acid (sp.gr. 1·16). After heating to dissolve any precipitate that may be formed the solution is cooled in water, stirring continuously with a thermometer, so that the temperature falls at the rate of about 1° C. per minute. If a turbidity appears before the temperature reaches 9° C., the usual confirmatory test for arachis oil must be applied; if the liquid remains clear at this temperature, arachis oil may be regarded as absent.

It is essential that the stirring should be continuous, since local cooling will cause the premature formation of a turbidity. For this reason the cooling water should not rise above the level of the liquid in the flask.

The turbidity temperature is best observed by looking through the liquid against a good light, and noting the temperature at which a definite precipitate first appears. The point is quite sharp and the personal error should not be more than ± 0·25° C.

Occasionally after acidification an oil gives a slight opalescence which is unaffected by warming. This may be disregarded, as it does not affect the true turbidity temperature.

Table I shows the results obtained with oils other than olive, almond, or apricot-kernel oils. The turbidity temperature of arachis oil itself is remarkably constant. Thirteen samples of various origins and grades all gave turbidity temperatures of 39° to 40° C. The test thus forms an excellent guide to the purity of arachis oil.

TABLE I

Oil	Clouding-point °C.
Arachis (13 samples)	39·0–40·0
Rape	22·5
Sesame	15
Cottonseed	13
Olive-kernel	10
Maize	7·5
Tea-seed A	9·5
Tea-seed B	2·5

In the absence of oils other than olive and arachis oils the turbidity temperature is a reliable quantitative measure of the arachis oil present. Fig. 2 shows the results obtained by taking the two olive oils of the series shown in Fig. 1 which gave the highest and lowest turbidity temperatures, and adding varying proportions of 13 different arachis oils. When the arachis oil is over 10 per cent. the turbidity temperature of the olive oil used does not exert any appreciable influence on the results.

ALMOND OIL.—The turbidity temperature of almond oil is lower than that of olive oil. Consequently there is no likelihood of a genuine almond oil giving a positive result when arachis oil is absent either with the B.P. test or with the modified test as described above. On the other hand, the clouding-point of almond oils is so low that the addition of 5 per cent. of arachis oil would escape detection. A series of almond and apricot-kernel oils has therefore been tested by the modified test, with and without the addition of 5 per cent. of arachis oil. The results are given in Table II.

TABLE II

CLOUDING-POINTS OF ALMOND AND APRICOT-KERNEL OILS

Oil		Clouding-point °C.	Clouding-point after addition of 5 per cent. of arachis oil °C.
Almond	A	1·0	5·5
	B	1·0	4·5
	C	1·5	4·5
	D	1·0	4·5
	E	0·0	4·5
	F	0·0	5·0
	G	—0·5	5·5
	H	—0·5	5·0
Apricot-kernel ..	J	—6·5	4·0
	K	—4·0	5·0
	L	—8·5	3·5
	M	—5·5	3·5

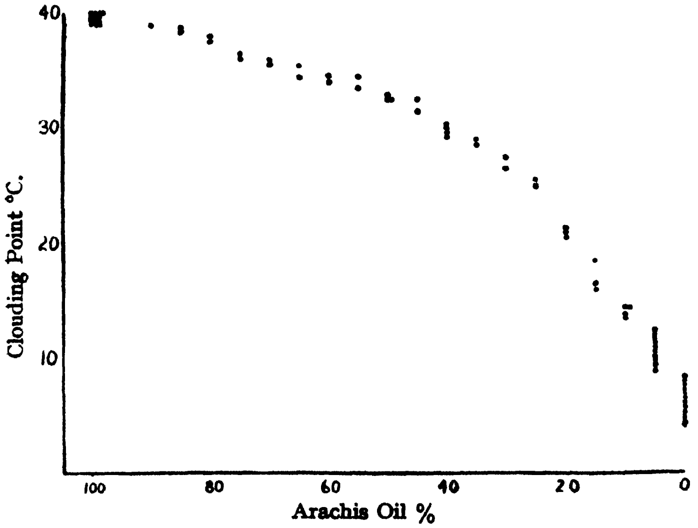


Fig. 2.

Oils A to E and J to M were authenticated samples and all English-pressed. Oil G was a French oil.

The addition of higher amounts of arachis oil to one of the genuine almond oils gave the following results:

Arachis oil added Per Cent.	Clouding-point °C.
0	1·0
5	4·5
7·5	9·5
10	15·0
20	20·5
30	26·5
50	32·5
75	36·5

It will be seen that when 10 or more per cent. of arachis oil is added, the results follow the curve in Fig. 2.

It seems necessary, therefore, when dealing with almond or apricot-kernel oils, to cool to 4° C. If a turbidity is formed, the confirmatory test must be carried out. Five per cent. of arachis oil will then be detected with certainty in the absence of other interfering oils.

I am indebted to Mr. E. R. Bolton, Messrs. Astor, Boisselier & Lawrence, Ltd., Leon Frenkel, Ltd., and Stafford Allen & Sons, Ltd., for kindly supplying samples of oil.

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DISCUSSION

Mr. E. M. HAWKINS said that he thought that the author's method might help in the detection of ground almonds. He had used the test on some oil extracted from Brazil nuts.

Mr. DAVIS mentioned that there were on the market olive oils, of North African origin, giving results below the B.P. titre. Had the author examined any of these oils?

Mr. C. E. SAGE said that the newer methods of preparing olive oil, by treating with chemical agents, oils with high acidities, yielded products which might be palatable and presentable at first sight, but they led to sophistication and admixture. Speaking generally, commercial olive oil had altered considerably in character in the last forty years. The Bellier test was not entirely reliable, and a complete Renard separation often yielded negative results, but some oils yielded crystals finally, which had to be considered arachidic acid, although they were derived from oils which were undoubtedly pure olive products. He had found that it was of the greatest importance to use pure alcohol, not industrial spirit, for the Bellier test.

Mr. E. R. BOLTON, in congratulating Mr. Evers on his communication, observed that until he had put before us the present test, analysts were in very many cases faced with conducting the full arachidic acid determination with its attendant melting-points, as being the only reliable way in which groundnut oil could be definitely detected and determined. The present test, however, clearly obviated the necessity of conducting this longer test so often.

Mr. Bolton also referred to the difficulties presented by "manipulated" oils and, as an example of such oils, cited the case of "green olive oils" which, having been extracted by carbon bisulphide, were very acid. The bulk of the free acids having been esterified with glycerin and the remaining acidity removed by distillation, after subsequent refining and bleaching an oil was prepared bearing resemblance to the original olive oil and introducing great difficulties in the test. He enquired if Mr. Evers had applied his new method to the detection of arachis oil in such reconstituted oils.

Mr. J. R. Nicholls asked if this test had been applied to other substances, such as hardened fats. It seemed that with such fats the gradual lowering of the temperature might cause a considerable positive reaction.

Mr. Evers, replying, said that he had not examined oil from Brazil nuts; the work had been done entirely on olive and almond oils. The presence of ground pea-nuts in ground almonds, however, could be detected very easily by this method. In reply to the question about North African oils, he said that one oil which gave a precipitate at 9° C. was a Tunisian oil; another Tunisian oil came out below 9° C. It was very easy to recognise these oils because of the heavy nature of the precipitate. He had not applied the test to hardened fats, but thought that it would not be satisfactory. He did not know whether any of the oils tested were "manipulated" oils, but a few of them might have been. The rate of cooling was a matter of great importance. He allowed the temperature to fall at the rate of 1° C. per minute, starting with warm water and then adding ice.

The Determination of Cyanide in Aqueous Extracts of Road Tars

By W. G. MOFFITT, Ph.D., A.I.C., and E. H. WILLIAMS, B.Sc., A.I.C.

(*Read at the Meeting, December 2, 1936*)

Introduction.—It has been shown by Southgate, Pentelow and Bassindale[1] that cyanide, in concentration above 0·01 part of CN per 100,000, is toxic to fish. Rain washings from recently tarred roads may gain access to fishing rivers, and it is important that they should not contain cyanide to this extent.

In the examination of a road tar the determination of cyanide is made on an aqueous extract, prepared under standard conditions (*vide infra*), and the concentration of cyanide in this extract is regarded as indicating the maximum that might be expected to occur in the rain washings from a recently tarred road.

The only method of determining cyanide found to be sufficiently sensitive is that described by Childs and Ball[2] (see also Weehuizen),[3] which is based upon the oxidation of phenolphthalin to phenolphthalein by cyanide in the presence of a cupric salt. This method is affected by the presence of phenolic compounds, and the following table shows how the presence of tar acids, prepared from a fraction of coal-tar creosote (205–230° C.), affects the test.

Childs and Ball (*loc. cit.*) state that by distilling under reduced pressure the quantity of phenols in the distillate will be reduced. When acidified solutions of potassium cyanide, containing appreciable quantities of tar acids, were distilled under reduced pressure, it was not found possible to obtain good yields of cyanide free from tar acids, and other methods were sought for preparing a pure solution of cyanide from the aqueous extract of a road tar.

TABLE I

THE EFFECT OF TAR ACIDS ON THE PHENOLPHTHALIN TEST FOR CYANIDE

Tar acids added (parts per 100,000)	0·0	0·05	0·10	0·50	1·00	2·00
Apparent cyanide (parts of CN per 100,000)	0·016	0·014	0·012	0·008	0·008	0·006

Attempts were first directed to removing the tar acids from the test solutions by extraction with solvents such as chloroform, carbon tetrachloride, benzene and petroleum spirit. When pure benzene or carbon tetrachloride is shaken with water the aqueous layer gives a positive reaction with the phenolphthalin reagent in the absence of added cyanide. Petroleum spirit has the opposite effect of slightly inhibiting the reaction. Chloroform is without effect on the phenolphthalin test, but it extracts a little of the hydrogen cyanide from the aqueous layer, particularly in the presence of a strong acid. When the neutral distillates from artificial mixtures of potassium cyanide and tar acids were extracted with chloroform the yields of cyanide obtained were consistently about 85 per cent. of the theoretical. When, however, this method was applied to neutral distillates from aqueous extracts of road tars, containing added quantities of cyanide, the cyanide determined by the phenolphthalin test varied from nil to 40 per cent. of the total (see Table II, col. 3).

TABLE II

Parts per 100,000

		Yield of cyanide	
1 No. of extract	2 Cyanide added to extract	3 (a) after extraction of distillate with $CHCl_3$	4 (b) after oxidation of distillate and further distillation
1	Nil	—	0·003
	0·008	0·003	0·003
2	0·003	Nil	0·0025
	0·008	0·001	0·005
3	0·0065	0·0015	0·0015

Since the final test is essentially an oxidation reaction, it seemed probable that, if the interfering substances in the aqueous extract could be preferentially oxidised before distilling off the cyanide, the resulting distillate would be free from interfering substances. Good results were obtained when artificial mixtures of cyanide and tar acids were oxidised with a slight excess of permanganate in the presence of phosphoric acid. When aqueous extracts of road tar, containing added quantities of cyanide, were oxidised in this way the yields of cyanide were often in excess of the theoretical, presumably owing to the oxidation of thiocyanate to cyanide. An alternative method was tried whereby the aqueous extract was first acidified with tartaric acid and then distilled. The distillate, which contained no thiocyanate, was oxidised at 20° C. with a slight excess of permanganate. A reducing agent, *e.g.* manganous chloride, was added before finally distilling off the hydrogen cyanide, in order to prevent the oxidation of cyanide by the excess permanganate at the boiling temperature. The results obtained by this method are given in Table II, col. 4.

These results (Table II, col. 4) suggest that there is an appreciable loss of cyanide on distilling the unoxidised tar extract. In order that the oxidation might be carried out on the tar extract before distillation, it was necessary to use an oxidising agent which would not oxidise the thiocyanate to cyanide.

Silver oxide proved to be a suitable oxidising agent when precipitated *in situ*. There is a loss of cyanide when silver oxide is precipitated from the nitrate, and better results are obtained by precipitating from silver acetate. Silver oxide will oxidise cyanide on boiling, and it is necessary to destroy excess of oxide before distilling, by adding a solution of stannous chloride. The distillate contains appreciable quantities of unoxidised tar acids and naphthalene, which must be removed by extraction with chloroform before applying the test.

Silver oxide has a slight oxidising effect on thiocyanate, which will only interfere, however, when the concentration of thiocyanate is more than a hundred times that of the cyanide. A modification of the method is described (*vide infra*) which gives reliable figures for cyanide in the presence of 1 part per 100,000 of thiocyanate. It is based on the precipitation of the thiocyanate as the silver salt in the presence of a little acid, which retards the reduction of the precipitated silver thiocyanate by the aqueous extract. The precipitated silver thiocyanate is not oxidised by silver oxide.

METHOD.—The aqueous extract of the road tar is prepared by shaking a known weight of the tar, approximately 100 g., spread over the bottom of a Winchester quart bottle, with 15 times its weight of cold, fully aerated, distilled water for 16 hours on a mechanical shaker at a temperature between 15–20° C. The extract is then filtered through a single 12-inch, fluted filter-paper.

The solutions required in the preparation of the solution for the test are as follows:—(*A*) A saturated solution of silver acetate, (*B*) a 1 per cent. solution of caustic soda, and (*C*) a 5 per cent. aqueous solution of stannous chloride containing 2·5 per cent. by vol. of conc. hydrochloric acid.

The distillation is carried out in a glass-stoppered distilling flask with a side-arm fitting by means of a ground-glass joint into a Liebig condenser. In place of the ground-glass joints rubber bungs covered with metal foil (tin or aluminium) may be used.

The filtered extract (250 ml.) is run into the distillation flask, and 50 ml. of saturated silver acetate solution are added. The contents of the flask are gently shaken while 12 ml. of 1 per cent. caustic soda solution are run in. The flask is then set aside for 15 minutes, after which 20 ml. of the stannous chloride solution are added and the distillation is begun. The distillate, about 75 ml., is made up to 100 ml. with distilled water, transferred to a dry separating funnel, and extracted three times with 10 ml. quantities of chloroform. The aqueous layer is transferred to a dry flask and, after standing for about 10 minutes, an aliquot portion, usually 50 ml., is taken for the test.

The following modification of this method should be used when the quantity of thiocyanate present is such as to give a distinct reddish colour on adding a drop of ferric chloride solution to 100 ml. of the extract slightly acidified with acetic acid. To 250 ml. of the filtered extract, in the distillation flask, are added 1 ml. of *N* acetic acid and 5 ml. of saturated silver acetate solution, and the flask is set aside in the dark for 30 minutes. A further quantity of 45 ml. of silver acetate solution is then added, followed by 12 ml. of 1 per cent. caustic soda solution and, after 15 minutes, 20 ml. of stannous chloride are added, and the solution is distilled and extracted as described above.

The reagents for the phenolphthalin test for cyanide are those given by Childs and Ball (*loc. cit.*, p. 298),[*] but a greater quantity of distillate is taken for the test.

The aliquot portion taken is diluted to 100 ml., and 1 ml. of the phenolphthalin reagent is added, followed by 2 ml. of 1 per cent. caustic soda solution. A red colour develops and is compared with that produced in solutions containing known quantities (0 to 0·015 parts of CN per 100,000) of cyanide treated in an identical manner.

The results (as parts per 100,000) obtained by this method with nine samples of road tars are given in Table III. The determinations were carried out on the fresh extracts, and, as the quantities of cyanide found were small, second determinations were made after addition of potassium cyanide, equivalent to 0·01 part of CN per 100,000, to the extracts. The figures in column 5 are the results obtained when the oxidation with silver oxide was omitted.

TABLE III

1 Tar examined	2 Cyanide added to aqueous extract	3 Tar acids found in extract	4 Cyanide found after oxidation, distillation and extraction	5 Cyanide found after distillation and extraction alone
A	—	0·4	Nil	—
	0·010		0·0075	—
B	—	1·8	0·0003	—
	0·010		0·009	—
C	—	2·4	0·001	—
	0·010		0·009	—
D	—	2·4	Nil	—
	0·010		0·008	0·0035
E	—	4·4	0·0005	—
	0·010		0·0095	0·004
F	—	5·0	0·0015	—
	0·010		0·0085	—
G	—	9·0	0·001	—
	0·010		0·009	—
H	—	28·0	0·001	—
	0·010		0·0095	0·001
I	—	40·6	0·001	—
	0·010		0·009	—

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[*] To prepare the reagent for the test, 10 ml. of a 1 per cent. solution of phenolphthalin containing 0·2 per cent. of sodium hydroxide are diluted to 50 ml. with a 2·5 per cent. solution of glycerol. To this are added 50 ml. of a 0·3 per cent. solution of copper acetate, and the whole is well mixed, filtered (if cloudy), and kept in a stoppered glass bottle.

The results obtained by the modified method, for extracts containing appreciable quantities of thiocyanate, are given in Table IV. As none of the extracts examined contained sufficient thiocyanate to test the method, potassium thiocyanate, equivalent to 1·0 part of CNS per 100,000, was added, and the test was applied to this mixture, with and without additional cyanide. The last two experiments, with solutions of thiocyanate in water, show that there is very little, if any, oxidation of the thiocyanate by this method.

TABLE IV

YIELDS OF CYANIDE OBTAINED IN THE PRESENCE OF THIOCYANATE

(Parts per 100,000)

Solution used	Thiocyanate added	Cyanide added	Cyanide found
Extract A	—	—	Nil
,,	1·00	—	0·0015
,,	1·00	0·01	0·011
Extract I	—	—	0·001
,,	1·00	—	0·0015
,,	1·00	0·01	0·008
Water	1·00	—	0·0007
,,	1·00	0·01	0·009

The method has been applied to artificial mixtures of cyanide with various phenols and the results are shown in Table V.

TABLE V

THE EFFECT OF ADDING PHENOLIC SUBSTANCES TO SOLUTIONS OF CYANIDE

1 Cyanide present (parts per 100,000)	2 Substance added	3 Quantity added (parts per 100,000)	4 Yield of cyanide after distillation and extraction Per Cent.	5 Yield of cyanide after oxidation, distillation and extraction Per Cent.
0·01	Purified tar acids from creosote	100	—	80
0·01		6	85	—
0·01	Phenol	100	—	80
0·01	*o*-Cresol	40	50	70
0·01	*p*-Cresol	40	60	80
0·01	1.2.3-Xylenol	40	65	80
0·01	1.3.5-Xylenol	40	70	80
0·01	Pyrogallol	40	Nil	75
0·01	Hydroquinone	5	Nil	75
0·01	Catechol	2	Nil	85
0·01	Catechol	10	—	60
0·01	Resorcinol	40	70	80
0·01	α-Naphthol	16	50	80
0·01	β-Naphthol	1	40	70
0·01	β-Naphthol	10	—	50

It will be seen that amounts up to 40 parts of the more common phenols per 100,000 are without appreciable effect on the method involving preliminary oxidation. The results in column 4 show the effects of these substances oxidation by silver oxide is omitted. The di- and tri-hydroxy phenols have the greatest effect. Catechol and β-naphthol, which when present in considerable quantity have a marked effect on the method, have been found in coal tars, but normally represent only a very small fraction of the total phenols (*cf.* Edwards[4] and Currey[5]).

SUMMARY.—Conditions are given whereby cyanide in aqueous extracts of road tars, in quantities of 0·01 part per 100,000, can be determined with reasonable accuracy. The tar acids are removed by oxidation with silver oxide, followed by distillation and subsequent extraction of the distillate with chloroform.

We wish to thank Dr. J. J. Fox, the Government Chemist, for permission to publish this work, and Mr. W. G. Adam, of the Gas, Light and Coke Company, for kindly supplying samples of road tars.

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DISCUSSION

The PRESIDENT said that this interesting paper was of importance in relation to the poisoning of fish. He asked whether it was a fact that this poisoning usually occurred when the tar was newly laid and again when the surface was breaking up and the road required re-tarring.

Mr. WILLIAMS replied that this was so.

Dr. H. E. COX remarked that the authors had made a notable contribution to a difficult problem. There was no doubt that the phenolphthalin test was the most sensitive one available for demonstrating the presence of cyanide, but it was not specific. The authors had been dealing with such extremely minute quantities as 1 in 200 millions; in streams where fish had died he thought that cyanide could be inferred from the red colour in the phenolphthalin test without other confirmatory tests.

Dr. MOFFITT replied that essentially the method had been worked out on tar. River water would first be distilled, and if one obtained a pink colour in the distillate he thought that one might attribute it to cyanide. He did not think that anything else in the distillate would give the reaction.

Mr. C. E. SAGE asked whether the authors had applied their method to the detection of traces of hydrocyanic acid in effluents, particularly those where land had been dressed with ammonium sulphate, or where there was drainage from piles of vegetable matter containing a cyanogenetic glucoside.

Mr. WILLIAMS replied that there had been cases of the poisoning of fish due to drainage from tarred roads and that the purpose of this test was to test the coal-tar itself before it was applied to roads draining into streams. The work was done in order to define a "non-toxic" tar conforming with a standard specification. It was not done from the point of view of investigating fish poisoning.

Mr. A. L. **Bacharach** asked whether the difference between the recovery of hydrocyanic acid alone, when it was 100 per cent., and in the presence of tar acids, when it was noticeably less, might not be due to some hydrolysis to formic acid.

Dr. **Moffitt** replied that there was a slight loss, amounting to 5 to 10 per cent. of the cyanides present, but they must remember that the acid was very weak. Undoubtedly, with strong acid, there was hydrolysis, but here the distillation was carried out in the presence of buffered acetic acid.

The Determination of Molybdenum in Cast Iron

By E. TAYLOR-AUSTIN, A.I.C.

Introduction.—The problem of suitable methods for the determination of molybdenum has been greatly accentuated in recent years by the increasing use of this element as an alloy addition to cast iron and steel. At the present time two methods are in general use for the determination of molybdenum in cast iron—the lead molybdate method and the sulphide method. Recently, following on the work of Knowles[1] and others, α-benzoinmonoxime has been introduced for the general determination of this element. The first published paper on the application of this reagent to cast iron appears to be that of Thompson and Stott.[2]

This work is a study of all three methods as applied to cast iron, and the conclusion to be drawn is that, although with certain modifications in procedure equally reliable results can be obtained by all the methods, the α-benzoinmonoxime method is the most satisfactory. Incidentally, the time taken for a determination by the latter method is 1½ to 2 hours, as compared with 4 to 5 hours by either of the other methods.

The Lead Molybdate Method.[3]—Long experience with this method, extending over a period of several years, has shown that when several determinations are made on the same sample of cast iron, the results do not always fall within the recognised limits of ± 0·02 per cent. of molybdenum, and, further, that the method occasionally yields low results. Also, the lead molybdate precipitate sometimes appears immediately on addition of the ammonium acetate solution and is granular, filtering well and scarcely adhering to the precipitation vessel, whilst on other occasions the precipitate does not appear until the solution has been boiled for several minutes after the addition of ammonium acetate solution, and is then in a finely divided state, tending to "creep" over the sides of the filter-funnel and adhering tenaciously to the vessel. This is not due to variations in the amount of molybdenum present, since duplicates of the same sample may exhibit these differences.

In this section an attempt is made to discover the cause of these irregularities and to prevent their occurrence by standardising or otherwise improving the conditions of precipitation. Since it is necessary to remove iron before the precipitation of molybdenum by this method, in the early stages of the work the conditions of precipitation from pure solutions were studied, a standard solution of pure molybdic oxide (AnalaR) in dilute sodium hydroxide being used.

THE EFFECTS OF AMMONIUM ACETATE CONCENTRATION.—The conditions of precipitation were made as nearly constant as possible in the following manner:—The equivalent of 0·68 per cent. of molybdenum (for a 1-gram sample) was added to a volume of 300 ml. of distilled water and the solution was made just acid to litmus with conc. hydrochloric acid and heated to boiling-point. Next 20 g. of ammonium chloride were added, and the boiling was continued for five minutes, after which 10 ml. of a 4 per cent. solution of lead acetate* were added, the resulting precipitate was just dissolved in hydrochloric acid, and 0·20 ml. in excess was added from a burette. The solution was again boiled and amounts of ammonium acetate solution,† varying from 5 to 80 ml., were added. After being boiled for 1 minute, or longer (if necessary to produce a precipitate), the solution was filtered, and the precipitate was washed with hot water, ignited and weighed. The results are shown in Table I.

TABLE I

Ammonium acetate solution added ml.	Weight of $PbMoO_4$ obtained (calculated $PbMoO_4$ from Mo taken 0·0260 g.) g.	Time taken for precipitate to appear after the addition of ammonium acetate Seconds
5	0·0260	2
10	0·0260	4
20	0·0258	6
30	0·0255	15
40	0·0240	25
50	0·0238	30
60	0·0230	55
70	0·0235	65
80	0·0230	75

It will be seen that under these conditions 5 ml. of ammonium acetate solution, as compared with 20 ml. recommended in the original method,[3] are sufficient to precipitate all the molybdenum added. As the quantity increases up to 80 ml. the results drop slightly, and it was also observed that the precipitates became less granular, although they showed no tendency to pass through the filters. Further, with 5 ml. of ammonium acetate solution the precipitates appeared almost immediately, but, as the amount of this reagent increased, the "time lag" of precipitation also increased, up to 75 seconds with 80 ml. of ammonium acetate solution.

THE EFFECTS OF HYDROCHLORIC ACID CONCENTRATION.—It was found that if the excess of hydrochloric acid, referred to above, was increased even by 0·10 ml., the amount of ammonium acetate solution required to produce a precipitate of lead molybdate within a given time increased very considerably, and the precipitates were less granular and required a much longer time for making their appearance. This effect is shown in Table II, and it will be seen that with an excess of 0·6 ml. of hydrochloric acid a precipitate could not be obtained in less than 60 seconds. Furthermore, with an excess of more than 0·3 ml. of acid the precipitates showed a pronounced tendency to pass through the filters. Thus, the best conditions appear to be established when 0·2 ml. excess of acid and 5 ml. of ammonium acetate solution are employed, the results obtained being consistently accurate within the limits of analytical tolerance.

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* Made by dissolving 40 g. of lead acetate in distilled water, just clearing the white precipitate formed with 30 per cent. acetic acid and diluting to 1 litre.

† Made by adding ammonium hydroxide (sp.gr. 0·880) to 30 per cent. acetic acid until neutral to litmus.

TABLE II

Hydrochloric acid added in excess ml.	Ammonium acetate required to yield a precipitate in less than 60 seconds ml.	Time for precipitation after addition of acetate Seconds
0·2	5	2
0·3	15	20
0·4	25	35
0·5	40	50
0·6	70	70

The conditions of precipitation are far evidently more exacting than the earlier literature on this method would suggest.

PRECIPITATION FROM ACETIC ACID SOLUTIONS.—In order to avoid, if possible, these rigid conditions and thus to simplify the method, a modification was introduced at this stage. It consisted in precipitating the molybdenum from solutions containing acetic acid, which is only slightly dissociated in solution, and thus avoiding the use of both hydrochloric acid and ammonium acetate. The equivalent of 0·68 per cent. of molybdenum was again added to 300 ml. of distilled water, but the addition of ammonium chloride was omitted. The solution was then made just acid to litmus with acetic acid (30 per cent.), and amounts of excess acid varying from nil to 80 ml. were added. It was then heated to boiling, and the molybdenum was precipitated by the addition of 20 ml. of lead acetate solution (4 per cent.). After being boiled for 1 minute the solution was filtered, and the precipitate was washed with hot water, ignited, and weighed as before. The results obtained are shown in Table III, and are seen to be very consistent, the greatest difference

TABLE III

Excess 30 per cent. acetic acid added ml.	Lead molybdate obtained (calculated $PbMoO_4$ from Mo taken 0·0260 g.) g.	Time taken for precipitate to appear after addition of lead acetate solution
Nil	0·0272	Immediate precipitation in every instance
10	0·0264	
20	0·0260	
30	0·0262	
40	0·0258	
50	0·0262	
60	0·0262	
70	0·0262	
80	0·0260	

between 8 determinations being less than 1 mg., with the exception of the first case, *i.e.* where little or no excess of acetic acid was present; under these conditions it appears probable that a little lead hydroxide was precipitated. Thus the whole of the molybdenum added is precipitated over a wide range of acetic acid concentrations.

When, however, the procedure described above was repeated with the addition of 20 g. of ammonium chloride the precipitates became less granular and showed a marked tendency to pass through the filters, more particularly on washing. In order to avoid this difficulty a little paper pulp was added prior to filtration. This reduced very considerably the tendency to "run through," although it did not prevent it entirely. It was found, however, that if a hot 2 per cent. solution of acetic acid was substituted for hot water as the washing medium, this difficulty was entirely removed, and the results became even more consistent than those obtained by the hydrochloric acid and ammonium acetate method with rigid control of conditions.

THE EFFECTS OF PHOSPHATE ION ON THE PRECIPITATION OF MOLYBDENUM IN ACETIC ACID SOLUTION.—The modified method described was then investigated more fully, particularly with reference to interference by the phosphate ion and the prevention of such interference by the addition of ammonium chloride. The same standard molybdenum solution as before was used, and to it was added a standard solution of pure (AnalaR) sodium phosphate. The precipitations were carried out in a volume of 300 ml. of distilled water containing 20 ml. excess of 30 per cent. acetic acid. No ammonium chloride was added at first. The precipitates were washed with hot 2 per cent. acetic acid solution, ten washes of which were sufficient to remove all the lead salts; the filtrates were tested from time to time with potassium dichromate solution. Since the true weight of lead molybdate, for any given amount of the standard solution of molybdenum added, was known accurately from previous experiments, the amount of interference due to phosphorus was calculated by difference.

TABLE IV

Phosphorus added Per Cent.	Lead molybdate obtained (calculated weight of $PbMoO_4$ 0·0260 g.) g.	Increase in weight due to phosphorus g.	Increase in weight due to 0·26 per cent. increase in phosphorus g.
0·26	0·0410	0·0150	—
0·52	0·0692	0·0432	0·0282
0·78	0·0970	0·0710	0·0278
1·04	0·1244	0·0984	0·0274
1·30	0·1525	0·1265	0·0281
1·56	0·1776	0·1516	0·0251

In the first series examined the molybdenum-content of the solution was kept constant at 0·68 per cent., and the phosphorus-content varied from 0·26 per cent. to 1·56 per cent., and the results are shown in Table IV. It will be seen that the weight of the precipitate increases with the amount of phosphorus present, and furthermore this increase is constant for every 0·26 per cent. added. The direct relationship observed between the phosphorus-content and the increase in weight of the precipitate, under the above-mentioned conditions, is so striking that it is unlikely that any lead phosphomolybdate is formed, so that one theory of phosphorus interference (*viz.* that it is due to the formation of phosphomolybdate) must be untenable.

In the second series examined, the amount of phosphorus present was kept constant at 1·0 per cent. and the molybdenum content varied from 0·13 per cent. to 2·66 per cent.; the results are given in Table V.

TABLE V

Molybdenum added Per Cent.	Calculated equivalent weight of $PbMoO_4$ g.	Weight of precipitate obtained g.	Increase in weight due to phosphorus g.
0·13	0·0051	0·1014	0·0963
0·27	0·0102	0·1067	0·0965
0·40	0·0152	0·1122	0·0970
0·53	0·0203	0·1177	0·0974
0·67	0·0254	0·1222	0·0968
1·33	0·0510	0·1480	0·0970
2·00	0·0764	0·2205	0·1441
2·66	0·1020	0·2602	0·1582

The weight of precipitate obtained, in excess of the calculated weight of lead molybdate, in this case, is seen to be constant up to a molybdenum-content of 1·33 per cent., but above this amount the weight of precipitate due to phosphorus increases with the amount of molybdenum present.

THE EFFECTS OF AMMONIUM CHLORIDE.—Again, the equivalent of 0·68 per cent. of molybdenum was added to a volume of 300 ml. of distilled water containing 1·0 per cent. of phosphorus, added as phosphate, and followed by amounts of ammonium chloride varying from 5 g. to 30 g. The precipitations were carried out exactly as before, and the results are shown in Table VI. It will be seen that with these amounts of molybdenum and phosphorus the addition of ammonium chloride has little or no effect until more than 15 g. have been added; 20 g. of the reagent reduce the interference due to phosphorus by about 25 per cent., whilst 25 or 30 g.

TABLE VI

Ammonium chloride added g.	Weight of precipitate obtained (calculated $PbMoO_4$ from Mo taken, 0·0260 g.)		
	P = 0·50 per cent. g.	P = 1·0 per cent. g.	P = 1·5 per cent. g.
5	0·0804	0·1572	—
10	0·0800	0·1588	—
15	0·0644	0·1470	—
20	0·0362	0·1170	0·1583
25	0·0259	0·0260	0·1054
30	0·0262	0·0262	0·0447
35	0·0260	0·0260	0·0258
40	0·0258	0·0262	0·0260
45	0·0264	0·0262	0·0259
50	0·0262	0·0258	0·0262

reduce it entirely and give a figure consistent with that obtained from phosphorus-free solutions.

These experiments were repeated with the same amount of molybdenum but with 0·5 per cent. and 1·5 per cent. phosphorus. Ammonium chloride in amounts up to 50 g. was subsequently added, and the results are shown in Table VI.

With a phosphorus concentration of 0·5 per cent. it will be observed that the theoretical figure is obtained again with 25 g. of ammonium chloride, but with 1·5 per cent. of phosphorus 35 g. are necessary.

Finally, since with more than 1·3 per cent. of molybdenum the extent of the phosphorus contamination increases with the addition of both molybdenum and phosphorus, another series was examined containing 4·0 per cent. of molybdenum and 1·5 per cent. of phosphorus. For these quantities 35 g. of ammonium chloride proved sufficient, although, as will be seen from the lower portion of Table VI, an excess of this reagent in no way impairs the results.

The modified method, which is described in detail below, was then applied to several samples of various types of alloy cast iron, and the results are shown in the Appendix.

THE MODIFIED LEAD MOLYBDATE METHOD.—Dissolve 2 g. of drillings in 35 ml. of conc. hydrochloric acid. When the action subsides, oxidise the solution with a few ml. of conc. nitric acid and boil off nitrous fumes; filter off the silica, graphite, etc., on a paper-pad filter and wash well with hot water. Transfer the residue and pad to a 750-ml. conical flask containing 150 ml. of 2 *N* sodium hydroxide solution and heat to boiling. Meanwhile, to the filtrate add dilute sodium hydroxide solution until the colour becomes a deep red-brown, but the liquid is still entirely free from precipitate. Warm this solution to about 60° C. and then run it slowly from a separating funnel into the flask containing the boiling sodium hydroxide solution and the original residue. The flask should be shaken continually throughout this procedure. When the whole of the solution has been introduced, shake the flask well, and transfer the contents to a 500-ml. measuring flask, dilute with hot water to the graduation-mark, and add a further 2 ml. of water to allow for the volume of the precipitated matter. Pour the solution back into the original flask, after shaking, and note its temperature. After allowing the precipitate to settle somewhat, filter off 250 ml. (equivalent to 1 g. of iron) through a double fluted filter-paper, and adjust the volume of this solution to the graduation-mark at the temperature previously recorded, *i.e.* at the temperature at which the solution was diluted to 500 ml. Transfer the solution to a 600-ml. beaker, and add 30 per cent. acetic acid until the liquid is just acid to litmus paper, followed by an excess of 20 ml. of this acid. Then add 25 to 30 g. of ammonium chloride, according to the phosphorus-content of the sample, heat the solution to boiling, add 20 ml. of 4 per cent. lead acetate solution (previously described), and continue boiling for 1 minute. Filter the liquid through a tight paper-pad filter and wash the precipitate 10 times with hot 2 per cent. acetic acid solution. Ignite the washed precipitate at a temperature not exceeding 600° C., and weigh as lead molybdate (which contains 26·16 per cent. of Mo).

Several of the precipitates obtained by this method from samples of cast iron were dissolved in 10 ml. of conc. hydrochloric acid, and the solutions were boiled, diluted and filtered. The precipitates were washed well with hot water, the filtrates were first made alkaline with sodium hydroxide and then acid with 30 per cent. acetic acid, exactly as before, and the molybdenum was precipitated with lead acetate solution as previously described. The weights of precipitates so obtained, with or without the addition of more ammonium chloride, were consistently the same as those of the original precipitates. Thus, provided that 25 g. to 30 g. of ammonium chloride are used, a re-precipitation is unnecessary.

THE SULPHIDE METHOD.[4]—This method is, of course, unaffected by phosphorus, but when molybdenum is precipitated in the presence of large amounts of iron (as in the analysis of cast iron) the precipitate obtained is invariably contaminated with iron. Purification may be carried out by any of the following methods:—

(i) Fuse the impure molybdic oxide with sodium carbonate, extract with hot water, filter off the ferric hydroxide so obtained, and ignite and weigh.

(ii) Boil the impure oxide with 20 ml. of 20 per cent. sodium hydroxide solution for 3 to 5 minutes, dilute to about 150 ml., and again boil for 5 minutes. Filter, wash the precipitate well with hot water, ignite and weigh the ferric oxide so obtained.

(iii) Acidify the filtrates obtained, after removal of iron, by either of the above-mentioned methods, with 30 per cent. acetic acid, add 20 ml. of acid in excess, and precipitate the molybdenum with lead acetate exactly as described in the modified lead molybdate method.

The weight of the iron residue obtained by either method (i) or (ii) is deducted from the weight of the impure oxide to obtain the true molybdenum figure. The method of treating the precipitate with 20 per cent. sodium hydroxide solution is much quicker than the fusion method and quite as satisfactory. Further, it avoids the use of platinum apparatus. It was found, however, when using this method, that there was a great tendency for some iron to pass through the filter. This may be avoided by diluting the solution well and boiling for about five minutes to coagulate the ferric hydroxide precipitate, as stated above.

The method of calculating the molybdenum percentage direct from the corrected weight of molybdic oxide obtained is open to serious objection. Owing to the high molybdenum content of the oxide (66·67 per cent.) any small errors in weighing or estimating the iron impurity to be deducted cause a large error in the final result. This can be overcome by using samples of 3 g. or more, but the precipitates of iron impurity obtained prove unwieldy by this method and it is far better to precipitate the molybdenum as molybdate, as stated in method (iii) (*supra*).

It is a rather significant fact that, in 14 of 16 determinations carried out by the sulphide method, which is generally reputed to yield low results, the actual figures obtained were slightly higher than those given by the modified lead molybdate method and the benzoin-oxime method for the same samples. The results for one particular case are shown in the Appendix.

The procedure described by Lundell, Hoffman and Bright,[5] in which the molybdenum is first oxidised with ammonium persulphate and then removed as sulphide in the presence of tartaric acid, was carried out a number of times on samples of 2, 3, and 5 g. Great difficulty was experienced in filtering off the molybdenum sulphide so obtained, and in every instance the precipitates fused on ignition, despite copious washing. In view of the close agreement obtained between results by the more simple sulphide method[4] and those by the other two methods cited, further work on the method of Lundell and his co-workers was abandoned.

THE α-BENZOINMONOXIME METHOD.—In mineral acid solution α-benzoinmonoxime yields precipitates with the following: molybdenum, tungsten, chromium (sexivalent), vanadium (quinquevalent), tantalum and niobium. Silicon interferes somewhat, and should be removed before estimating any of the above-mentioned elements.

The following metals are not precipitated: silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, aluminium, iron, titanium, zirconium, chromium (tervalent), vanadium (quadrivalent), cerium, uranium, nickel, cobalt, manganese, zinc, selenium, tellurium, rhenium, ruthenium, rhodium, osmium, indium and platinum.[6]

The α-benzoinmonoxime method possesses several marked advantages over the two methods already studied:

(i) Samples of 3 g. or more may readily be dealt with; the sodium hydroxide separation incorporated in the lead molybdate method is impracticable if more than 2 g. of iron are present.

(ii) It provides a complete separation, in one operation, of molybdenum from all elements commonly found in cast iron, with the exception of silicon, which is, however, readily removed prior to precipitation. Thus nickel, titanium, phosphorus, manganese and iron do not yield precipitates under any conditions; chromium and vanadium are not precipitated in their reduced states, nor copper in acid solutions.

(iii) In the lead molybdate method a sodium hydroxide separation is necessary to remove iron, whilst if vanadium is present, special treatment, involving the use of manganese chloride, must be adopted; in the sulphide method the molybdenum is still associated with the other elements of the hydrogen sulphide group, *e.g.* copper, arsenic, etc. The use of α-benzoinmonoxime thus avoids many tedious separations, especially when dealing with complex alloy cast irons.

CONDITIONS OF PRECIPITATION.—*Permissible acidity.*—In order to prevent the interference of certain elements, the solution from which the molybdenum is precipitated must be distinctly acid. In the method given in detail later, a sulphuric acid solution is employed, but, should the presence of this acid prove objectionable, equally good results may be obtained with hydrochloric or nitric acid solutions of the same concentration by volume. Tartaric acid should be absent, as the precipitations are incomplete in its presence. Hydrofluoric acid is also to be avoided. In the method published by Thompson and Stott[2] insufficient attention is paid to the acid concentration of the final solution. The actual figures given by these authors are incomplete, but a rough approximation shows the concentration of sulphuric acid to be between 8 and 10 per cent. by vol. By keeping the acid concentration down to 5 per cent., or slightly less, better results were obtained, and the precipitates were contaminated by only very small quantities of iron.

Precipitation temperature.—The temperature of the solution at the time of precipitation should be below 10° C., for above this temperature there is a danger of reducing sexivalent molybdenum before it is precipitated. Even at the lower temperatures it is advisable to add a little bromine water to minimise the risk of reduction.

Amount of reagent required.—About three times the theoretical amount, as determined by the relation $1Mo \equiv 3C_6H_5.CH(OH).C{:}(NOH).C_6H_5$, is necessary for complete precipitation.

Time taken for complete precipitation.—Experiments have shown that precipitation is complete almost as soon as the reagent is added, but it appears advisable to allow the solutions to stand for about 10 minutes with occasional stirring. If the precipitate is allowed to remain in contact with the solution for more than 30 minutes there is a tendency towards low results.

The reagent.—In the early stages of this work an alcoholic solution of α-benzoinmonoxime was employed, but it was subsequently found that solutions in acetone yielded equally satisfactory results, and this latter solution was therefore adopted as standard.

The published method,[2] previously cited, suggests the use of 1 g. samples, but in view of the high molybdenum-content of the oxide (mentioned under the sulphide method) samples of from 2 to 5 g. were employed. It was found that, for general use, samples of 3 g. were most satisfactory and convenient.

The method finally adopted was as follows:—Dissolve 3 g. of the sample in 35 ml. of nitro-sulphuric acid (made by adding 250 ml. of conc. sulphuric acid and 300 ml. of conc. nitric acid to 1500 ml. of distilled water) as in the estimation of silicon, evaporate the solution to dryness, and heat the residue at 250° to 300° C. for 10 minutes. In some instances it has been found that no fumes are evolved at this stage, but this in no way affects the results. (If more sulphuric acid is added and the final solution is diluted to adjust the acid concentration to 5 per cent., the resulting volume of solution proves rather unwieldy.) Allow the residue to cool somewhat, add 100 ml. of hot 5 per cent. sulphuric acid, and boil the solution until all salts have dissolved. With some cast irons containing chromium it is difficult to dissolve the salts, and boiling may have to be continued for as long as 10 minutes. Filter off graphite, silica, etc., and wash the residue with three 15-ml. portions of 5 per cent. sulphuric acid and then six times with hot water. To the filtrate add 10 to 15 ml. of sulphurous acid, and boil for about 10 minutes to expel sulphur dioxide. Dilute the solution to 250 ml., cool to a temperature of 5° to 10° C., add, with constant stirring, 10 ml. of the reagent (a 2 per cent. solution of α-benzoinmonoxime in acetone) followed by sufficient bromine water to colour the solution a pale yellow, and finally add a further 5 ml. of the reagent. Allow the solution to stand at 5° to 10° C. for 10 to 15 minutes with occasional stirring, add a little ashless paper-pulp, and filter through a No. 40 Whatman filter-paper. The precipitate is more readily filtered off on a filter-paper than on a paper-pad; if suction is applied to the latter type of filter, filtration almost ceases. Wash the precipitate well with a 1 per cent. solution of sulphuric acid containing 2·5 per cent. of the reagent at a temperature of 5° to 10° C. Dry the washed precipitate and carefully ignite at as low a temperature as possible until all the organic matter has been burnt off and then at a temperature not exceeding 500° C. On no account should the temperature be allowed to rise above this limit, owing to the volatility of the molybdic oxide. This proves a frequent source of error. The molybdenum is finally weighed as molybdic oxide, which contains 66·67 per cent. Mo.

The method requires careful manipulation if correct results are to be obtained, and the conditions given should be strictly adhered to. With 3-gram samples it has been found that, with the above-mentioned acid concentration, the contamination by iron of the precipitates obtained is negligible for routine purposes, being consistently less than 1 mg. If desired, a re-precipitation may be made by dissolving the precipitate in sodium hydroxide solution and precipitating the molybdenum as lead molybdate, as described under the purification of ignited sulphide precipitates.

In determining small amounts of molybdenum (below 0·1 per cent.) some iron is invariably precipitated, and it is best to dissolve the ignited precipitate in sodium hydroxide solution, and then to acidify with sulphuric acid and determine the molybdenum colorimetrically by adding stannous chloride and potassium thiocyanate solutions.[7]

Subsequently, over 100 determinations were carried out by this method, and it was found that the lower the temperature at which precipitation is made, the less the contamination due to iron; if precipitations are made in an ice-bath, only the merest trace of iron is carried down (less than 0·1 mg.).

I wish to express my thanks to the Director and Council of the British Cast Iron Research Association for permission to publish this work.

APPENDIX

	Samples examined	Modified lead molybdate method Mo Per Cent.	α-Benzoin-monoxime method with direct weighing as MoO_3 Mo Per Cent.	Benzoin-monoxime method with re-precipitation as $PbMoO_4$ Mo Per Cent.	Sulphide method Mo Per Cent.
A	B.C.S. sample K	0·37	0·35	0·35	0·39
	(Molybdenum cast iron)	0·38	0·36	0·34	0·39
	Ni, 1·73 per cent.	0·37	0·39	0·37	0·38
	Cr, 0·41 ,,	0·34	0·36	0·36	—
B	U.S. Bureau of Standards	0·70	0·70	0·70	—
	Sample. Mo, 0·687 per cent.	0·67	0·65	—	—
C	Crankshaft	0·89	0·87	0·87	0·86
	(Cast iron)	0·89	0·87	0·86	0·86
	Ni, 0·16 per cent.	0·89	0·89	0·86	0·87
	Cr, 0·53 ,,	0·89	0·88	0·87	0·86
		0·88	—	—	—
		0·88	—	—	—

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BRITISH CAST IRON RESEARCH ASSOCIATION
21–23, ST. PAUL'S SQUARE
BIRMINGHAM, 3

A Colorimetric Method for the Determination of Traces of Phenol in Water

G. U. HOUGHTON, M.Sc., F.I.C., AND R. G. PELLY, F.I.C.

IT has long been known that extremely minute quantities of phenolic substances may give rise to an "iodoform" taste in water which is subsequently purified by chlorination, and that over 10 p.p.m. of tar acids in a river water may prove toxic to fish-life.

Several colorimetric methods have therefore been proposed for the determination of phenols in water. Perhaps the best known of these is the method of Fox and Gauge,[1] which depends on the formation of a yellow or red dyestuff when phenol is coupled with diazotised sulphanilic acid. Other workers (*e.g.* Hinden-Splittgerber,[2] Hilpert and Gille,[3] Folpmers[4]) have employed similar methods, using *p*-nitraniline in place of sulphanilic acid. Baylis[5] has based a procedure on the Gibbs indophenol test,[6] in which the phenol is converted into a blue indophenol by reaction with 2:6-dibromo-quinonechloroimide. The Folin and Denis method[7] employs phosphotungstic-phosphomolybdic acid, which gives a blue colour with phenol, but it has been stated[8] that the test is not specific for aromatic compounds. The Millon reagent has also been employed for the detection of phenols (Bach[9]).

Probably the most satisfactory of these methods is that of Fox and Gauge, but the reagent gives a slight yellow colour with certain vegetable substances present in surface waters, and, being applied in alkaline solution, difficulties may arise through precipitation of calcium and magnesium salts. To overcome these objections the authors direct that the phenol should be extracted with chloroform, and washed therefrom with alkali, and the test applied to this alkaline solution. The Baylis method suffers from the disadvantage that the colour of the indophenol develops only slowly with small concentrations of phenol, and the test-solutions must be allowed to stand for several hours, or preferably overnight, before matching. There is also a sharply optimum *p*H range for maximum colour production, and sample and standard must be buffered so as not to differ from a *p*H of 9·6 by more than 0·2 unit. The sensitivity of the method is, however, great—about 0·01 p.p.m. for a direct test. A distillation technique is also described by which it is claimed that 0·001 p.p.m. of phenol may be determined, but, as Fox and Gauge[1] point out, distillation is open to the objection that some of the higher phenols are not volatile, while phenol itself only distils over slowly.

In an attempt to overcome these disadvantages, we have developed a new procedure in which the phenol is converted into an indophenol by the well-known method of oxidation with hypochlorite in the presence of dimethyl-*p*-phenylenediamine. In this case the indophenols produced are readily soluble in organic solvents (unlike the indophenols produced by the Gibbs reagent) so that the sensitivity of the method may be increased by extracting the indophenol with carbon tetrachloride and matching the extracts. In tests on 200 ml. of a sample the sensitivity of the method is about 0·01 p.p.m. of phenol. The method has the advantage of quickness, and the *p*H of the solution is a far less critical factor than when the quinonechloroimide is used. Actually, satisfactory development of colour takes place provided that the *p*H is between approximately 7·0 and 8·5, and it is advisable to buffer both standard and sample with a small quantity of sodium bicarbonate before testing.

Table I shows the colour of the indophenol solutions obtained from a few of the higher phenols by the use of this method; the solutions tested contained 1 p.p.m. of the phenol in tap water.

TABLE I

Phenol	Aqueous solution of indophenol	Carbon tetrachloride solution of indophenol
Phenol	Blue	Purple
o-Cresol	Deep blue	,,
m-Cresol	,, ,,	,,
p-Cresol	No reaction	—
m-Xylenol	Pale blue	Blue
α-Naphthol	Purple	Purple
β-Naphthol	Very pale green	Green
o-Chlorophenol	Turquoise blue	Blue
p-Chlorophenol	Pale blue	Pale purple
Trichlorophenol	No reaction	—

As with the Gibbs reagent, *p*-cresol does not give the reaction. The sensitivity of the test varies for different phenols, and for those tested it is greatest with *o*-cresol and least with β-naphthol. The only interfering substances so far encountered are the primary aromatic amines, which give coloured indamines with the reagent. Aniline, *o*-toluidine, *m*-toluidine, *m*-xylidine and the naphthylamines all react, but, with the exception of α-naphthylamine, the sensitivity is only about 1 p.p.m., which is much less than with the phenols. α-Naphthylamine may be recognised by the magenta-coloured solution which its indamine forms in carbon tetrachloride solution. Except in special cases, these amines are unlikely to be present in water unless accompanied by a large excess of phenol.

SOLUTIONS REQUIRED.—(i) *p*-Nitrosodimethylaniline, 0·1 per cent. in distilled water. The nitroso compound is dissolved by gradual addition to the water which is just below boiling-point; the solution is cooled and filtered, and will then keep for at least a week. The diamine reagent is prepared immediately before use by shaking the above-mentioned solution with a large excess of zinc dust until decolorisation is complete, the reduction being hastened by the addition of one drop of 10 per cent. copper sulphate solution for every 10 ml. of reagent. The excess of zinc is filtered off, and the filtrate then usually exhibits a pale pink tinge which does not appear to be detrimental.

(ii) Sodium bicarbonate: a 5 per cent. aqueous solution.

(iii) Sodium hypochlorite solution containing 0·05 per cent. of available chlorine.*

(iv) Standard phenol solution: 1 ml. = 0·01 mg. of phenol. The solution should be prepared immediately before use by dilution of a 0·1 per cent. solution of phenol which has been standardised against 0·1 *N* bromide-bromate solution. In practice it has been found that the tint of the indophenols produced from polluted waters has generally been sufficiently near that of a phenol standard for satisfactory matching, but in certain cases it may be preferable to employ ortho- or meta-cresol or xylenol as standards.

METHOD.—The sample should be examined as soon as possible after collection, since dilute solutions of phenols are liable to undergo biological decomposition. It should be filtered if at all turbid.

(A) *When the phenol-content of the sample is greater than* 0·15 *p.p.m.*—It is always preferable to make a preliminary test in order to ascertain the approximate quantity of phenol present and the volume of hypochlorite solution which is required. To 100 ml. of the sample in a small flask are added 2 ml. of the bicarbonate solution, followed by 2 ml. of the filtered diamine reagent, and the hypochlorite is then run in gradually from a burette, with gentle agitation. The first addition of hypochlorite results in the formation of a pronounced pink colour, but this is completely discharged on adding more hypochlorite, and in the presence of over 0·10 p.p.m. of phenol the colour of the solution changes to pure blue, owing to the formation of indophenol. No further addition of hypochlorite should be made once the solution is free from any red tinge, since a large excess of chlorine would tend to bleach the blue colour.†

The approximate phenol-content of the sample is then determined by matching the blue colour obtained against the colour produced in a similar manner by a known volume of standard phenol solution, the matching being made in Nessler glasses by the balancing-column method.

To determine the phenol-content accurately, the sample is diluted so as to contain 0·15 to 0·30 p.p.m. of phenol and treated with diamine reagent and hypochlorite in the manner described above, and the blue colour is then matched exactly against one of a set of appropriate phenol standards. The colours are matched after standing for 2 to 3 minutes.

(B) *When the phenol-content is less than* 0·15 *p.p.m.*—The following procedure may also be employed when the sample is highly coloured. To 200 ml. of the sample in a separating funnel are added 4 ml. of the bicarbonate solution followed by 4 ml. of the diamine solution. The correct quantity of hypochlorite solution (already ascertained from a preliminary test) is then gradually run in, so as just to discharge the pink colour which first appears. The indophenol is now extracted with two 10-ml. portions followed by one 5-ml. portion of pure carbon tetrachloride, and the extracts are dried by the addition of a little anhydrous sodium sulphate. The solution is finally extracted with a further 5 ml. of tetrachloride, which is also used to wash out any indophenol remaining in the sulphate used for drying the previous extracts. The dry extracts are made up to a definite volume and matched in narrow Nessler glasses against standards prepared in precisely the same fashion. When the indophenol is extracted by this method care should be taken to ensure that sufficient hypochlorite has been added, since otherwise there is a risk of extracting incompletely chlorinated diamine, which is apt to impair the colour of the indophenol solution.

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* The hypochlorite employed in the present work was prepared from sodium carbonate and bleaching powder (sodium carbonate, 60 g.; bleaching powder, 40 g.; water, 400 ml.), the filtrate being diluted so as to contain 0·05 per cent. of available chlorine.

† It has been found that actually the titration with hypochlorite may be overdone by at least 0·5 ml. without materially affecting the results.

The following results were obtained when using the method for the determination of phenol which had been added to distilled water and to impure river water (hardness 280 p.p.m.: colour, 30 units, American Public Health Association). The quantities of phenol added were unknown to the operator and visual matching was carried out in Nessler tubes.

TABLE II

Sample	Phenol added p.p.m.	Phenol found p.p.m.
River water	0·025	0·024
,,	0·065	0·068
,,	0·095	0·080
,,	0·135	0·14
,,	0·170	0·15
,,	0·33	0·31
,,	0·53	0·50
,,	0·67	0·64
,,	0·87	0·90
Distilled water	0·15	0·15
,,	0·30	0·30
,,	0·50	0·50
,,	0·73	0·73
,,	0·90	0·86

In conclusion, we wish to thank Mr. L. D. K. Morrison for his assistance during the course of this work, and the Chairman and Directors of the Southend Waterworks Company for their permission to publish the results.

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LABORATORY
SOUTHEND WATERWORKS COMPANY
LANGFORD, ESSEX

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

AN UNUSUAL ADULTERANT FOR PEPPER

From one of our Authorities we recently received four sealed samples of pepper, which we will designate A, B, C and D; the last was described as "Pepper" and the others as "White Pepper." Microscopically, they appeared to be perfectly genuine; D contained more husk than the others.

The ash of these samples we found to be 4·29, 1·02, 0·98, and 4·70 per cent., respectively, and when re-carbonated they were 8·28, 1·24, 1·22, and 8·78 per cent.

We examined the ash of samples A and D, in both of which we found notable amounts of magnesia, which we determined quantitatively, and found in A 7 per cent. and in D 8 per cent. (calculated as $MgCO_3$).

The two samples were further examined and found to contain magnesium carbonate. This adulterant, in these amounts, is difficult of detection, as it is likely to be missed in the microscopical examination, and, unless the ash is re-carbonated, its amount might not arouse suspicion, particularly if the sample be described as "pepper."

The appearance of these two samples was excellent—that of white peppers in fact, but on removing the magnesium carbonate by dilute acids, the original pepper in D was seen to be distinctly inferior to that in A, as containing considerably more husk.

Not only does the addition of magnesium carbonate improve the appearance of the pepper, but its employment presents some temptation, as its cost is about one-third that of pepper.

J. T. Dunn
H. Charles L. Bloxam

Public Analysts' Laboratory
10, Dean Street
Newcastle-upon-Tyne, 1

THE PHOSPHATASE TEST

We have been carrying out the phosphatase test upon samples of pasteurised milk for two local authorities in London for the last six months.

So far as our results indicate, we have found the test extremely useful, not only in detecting gross errors in pasteurisation, but also in revealing small errors in technique—such as insufficient period of heating (less than half-an-hour) or heating slightly below 145° F. Recently we have had an interesting border-line case which clearly indicates the utility of the test in this direction. A particular sample gave a blue value of 3·3 Lovibond units and we reported that the results indicated a slight error in technique. The sanitary inspector, therefore, checked the temperature records of the particular dairy in question, and he was able to ascertain that on that particular day the temperature of pasteurisation was near 140° F. for a considerable time.

Regarding the method of carrying out the test, we have also noticed a number of points emphasised in the paper by Anderson, Herschdörfer and Neave (see p. 86). There is one point, however, about the "buffer substrate" which is worth noting. We have used, throughout, tablets supplied by the British Drug Houses, and have found them quite satisfactory. These tablets are particularly useful when one has to make a few tests intermittently, and not regularly from day to day, because a fresh solution of the buffer substrate can be easily prepared in a few minutes by dissolving one tablet in 50 ml. of chloroform water.

Finally, we would refer to the confusion that seems, from our experience, to exist in some quarters concerning the use of this test as an index of the bacteriological condition of milk. Some appear to think that if a sample passes the phosphatase test, it must necessarily be bacterially clean. Whilst this is true in most instances, it is important to emphasise the point that the phosphatase test gives no indication of any bacterial contamination that milk may receive *after* pasteurisation. For example, if a sample has been correctly pasteurised and then put into dirty containers or has otherwise been handled in some unhygienic way, it will still pass the phosphatase test, so that one cannot rely wholly on this test by itself and a bacteriological examination becomes necessary to guard against this contingency. The two in combination—*i.e.* the phosphatase test and bacteriological examination—afford as effective a control of pasteurised milk supply as we seem likely to get at present.

F. W. Edwards
H. R. Nanji

Analytical Laboratories
32, Leicester Square
London, W.C.2

A METHOD FOR THE ANALYSIS OF CARBONATE, HYDROXIDE CYANIDE MIXTURES*

The results given below and the method of obtaining them may be of interest to analysts faced with similar problems the solution of which is perhaps at first sight not self-evident. The solution, of which an analysis was required, was a cadmium plating bath and contained cyanide, hydroxide, carbonate, cadmium and alkali metal "ion." The method adopted was as follows:

(*a*) Carbonate was determined by treating the solution with a solution of barium nitrate, filtering off the barium carbonate, washing, dissolving in a measured excess of standard hydrochloric acid, and titrating the excess. Addition of barium nitrate and the filtering and washing operations were carried out in an atmosphere free from carbon dioxide.

(*b*) Hydroxide was determined by treating the filtrate from (*a*) with a solution of silver nitrate and ammonium nitrate and then with a measured excess of standard sulphuric acid, filtering and washing, treating the filtrate with 2 to 3 g. of sodium chloride, again filtering and washing, and titrating the excess acid back with standard alkali, using methyl red as indicator.

(*c*) Cyanide was determined on a fresh portion of the sample gravimetrically by adding ammonium nitrate and silver nitrate, making faintly acid with nitric acid, filtering off the precipitated silver cyanide, washing, drying and weighing.

†(*d*) Alkalinity due to hydroxide and carbonate combined was determined by adding silver nitrate and ammonium nitrate, followed by a measured excess of standard sulphuric acid, filtering and washing, adding an excess of sodium chloride, again filtering and washing, and titrating back the excess acid, using methyl red as indicator.

†(*e*) Total alkalinity was determined by adding an excess of standard sulphuric acid, boiling, cooling and titrating back the excess acid.

(*f*) Cadmium was determined as usual by precipitation as sulphide and weighing as sulphate.

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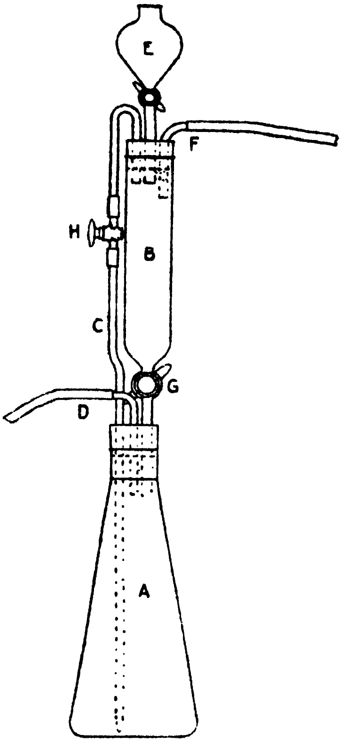
* Communication from the Research Department, Woolwich.

† Check determination.

The only part of the method which calls for comment is the precipitation, filtration and washing of the barium carbonate precipitate in (*a*). The apparatus used was the percolator already described in this journal (Evans, ANALYST, 1926, 51, 230). A pulp filter was placed in the bottom of the main funnel B. The tube D was connected to a soda-lime tower and tube F to the pump, and a slow stream of air was drawn through until carbon dioxide had been removed from the apparatus. The pump was then detached and the tube F closed; the sample was run in through the top funnel E on to the filter (the tap G of the main funnel being closed) and rinsed in with a little water (care being taken not to admit any air); the barium nitrate solution was added in the same way. When precipitation was complete the tap G was opened and the solution allowed to filter into the flask; if there was any haze in the liquid (showing that barium carbonate had been carried through the filter), the filtrate was retransferred to the main funnel by closing the tap G and re-attaching the pump to F, and was then re-filtered. When the filtrate was bright the precipitate was washed by admitting quantities of cold boiled-out water through the top funnel and allowing them to run through the filter. Solution of the barium carbonate was achieved by disconnecting the apparatus, closing the tap G, running the required amount of acid into the main funnel, stirring and digesting. The initial precipitation can, if required, be carried out in the flask, both sample and precipitant being filtered into it; in that case the liquid and precipitate are transferred to the top funnel, as outlined above, and the remains of the precipitate rinsed up with repeated filtrations and transferences. The tap H of the return tube was allowed to remain open throughout the operations.



The results obtained were as follows:

		Grams per litre		NaOH equivalent
(*f*)	Cd	42·9		
(*c*)	CN'	48·4		
(*b*)	OH' expd. as NaOH	21·2	≡	21·2
(*a*)	CO''_3 expd. as Na_2CO_3	90·0	≡	68·0
				89·2 { alkalinity calc. from $OH' + CO''_3$
(*d*)	Alkalinity due to $OH' + CO''_3$ expd. as NaOH	—	=	89·0 (determined)

		Determined	Calculated from $CN' + OH' + CO''_3$
(*e*)	Total alkalinity expd. as no. of ml. $N/10$ acid required for 1·00 ml. of sample	41·50	40·95

The calculated total alkalinity includes, of course, the combined errors on the three determinations.

B. S. EVANS

THE DETERMINATION OF PHOSPHORUS IN SILVER PHOSPHATE

RECENTLY Bloom and McNabb[1] published a method for the volumetric determination of silver by titration with potassium iodide, using ceric ammonium sulphate and starch as indicators. This procedure has been extended to the determination of phosphorus after the precipitation of silver phosphate and its subsequent solution in nitric acid. This method gives excellent results, but interfering ions, such as those of arsenate, tungsten, sexivalent chromium and molybdenum, must be absent. The use of the potassium iodide method is advantageous, since it eliminates frequent standardisations. The standard solution may be prepared by direct weighing.

In precipitating silver phosphate it is necessary to maintain the proper *p*H. Kolthoff[2] points out that good results may be obtained by precipitation of the silver phosphate in a buffered solution. He also states that if the silver phosphate is dissolved in nitric acid and the silver determined by the Volhard procedure, low results are obtained, owing to the loss of silver phosphate by washing. The procedure recommended is similar to that given by Kolthoff.[2] The precipitate was washed, however, with a saturated silver phosphate solution. Results were low unless this modification was employed.

Procedure.—Weighed samples of pure, dry potassium dihydrogen phosphate were dissolved in about 100 ml. of water. Two to three drops of methyl orange indicator were added. (If free acid is present it is necessary to add alkali.) A 5 to 10 ml. excess of 0·1 *N* silver nitrate solution was added with stirring, followed by the dropwise addition of 8 ml. of a saturated sodium acetate solution. After the solution had been filtered, the precipitate was washed by decantation with saturated silver phosphate solution until a portion of the filtrate gave only a faint turbidity when tested for silver ions. The precipitate was then dissolved off the filter with approximately 30 ml. of hot 2 *N* nitric acid, washed with hot water and collected in the original beaker. Sufficient 6 *N* sulphuric acid was added to make the solution about 1 to 2 *N* with respect to this acid, and then 3 drops of 0·1 *N* ceric ammonium sulphate solution and 5 ml. of 0·5 per cent. starch solution. The volume at this point was 125 to 165 ml. The silver was then titrated with 0·1 *N* potassium iodide solution to a permanent blue-green end-point. A blank test was made, omitting the silver nitrate. It required about 0·15 ml. of the potassium iodide solution.

The following results were obtained:

Potassium dihydrogen phosphate g.	Phosphoric anhydride calculated g.	Phosphoric anhydride found g.	Difference g.
0·2000	0·1043	0·1042	−0·0001
0·2015	0·1051	0·1050	−0·0001
0·2112	0·1102	0·1103	+0·0001
0·2020	0·1054	0·1052	−0·0002
0·2008	0·1050	0·1048	−0·0002
0·2027	0·1058	0·1056	−0·0002
0·1013	0·0529	0·0528	−0·0001

SUMMARY.—A satisfactory volumetric method for the determination of phosphorus in silver phosphate has been described. After solution of the silver phosphate in nitric acid, the silver is titrated with potassium iodide, ceric ion and starch being used as internal indicators.

Washing the silver phosphate precipitate with water yields low results. This may be avoided by washing with a saturated silver phosphate solution.

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N. RUBIN
W. N. MCNABB

THE JOHN HARRISON LABORATORY OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, U.S.A.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1936

OF the 1295 samples submitted by the Food and Drug Inspectors, only one was bought formally.

WHITE CHOCOLATE.—Three samples of a new type of confectionery were taken. These were sold as "White Chocolate" and were composed of a mixture of cocoa butter, dried milk and sugar. True chocolate, of course, should contain cocoa powder and should be of a brown colour. The name "White Chocolate," is therefore, a contradiction in terms. The label of one of the samples gave the composition of the article, and no action was taken in this case. The labels on the other samples gave no indication of the constituents, and both the firms concerned were communicated with. As a result, the name of each article was changed to "Milky Block," which does not suggest any affinity with chocolate.

TABLE CREAM.—A sample, labelled "Thick Rich Table Cream," contained only 21 per cent. of fat, whereas ordinary dairy cream contains an average of about 50 per cent. The use of the adjective "Rich" in the description of this sample is certainly not justified, and the vendor agreed to leave it out in future.

H. H. BAGNALL

Official Appointments

THE Minister of Health has approved the following appointments:—

REGINALD FRANK WRIGHT as a Public Analyst for the County Borough of Brighton, in addition to Samuel Allinson Woodhead (November 10th, 1936).

WILLIAM WILDERS TAYLOR as a Public Analyst for the County Borough of Nottingham, from January 1st, 1937, in place of S. R. Trotman, retiring (December 4th, 1936).

REGINALD FRANK WRIGHT as a Public Analyst for the County of West Sussex, in addition to Samuel Allinson Woodhead (December 9th, 1936).

ALEXANDER HENRY MITCHELL MUTER as a Public Analyst for the County of the Parts of Kesteven (Lincolnshire), in place of B. Henry Gerrans (deceased) (December 12th, 1936).

THOMAS MCLACHLAN as a Public Analyst for the Borough of Chelsea, in place of B. Henry Gerrans (deceased) (December 17th, 1936).

WILLIAM WILDERS TAYLOR as a Public Analyst for the Borough of Newark-on-Trent, from January 1st, 1937, in place of S. R. Trotman, retiring (December 17th, 1936).

DANIEL DONALD MOIR as a Public Analyst for the County of Surrey, in place of T. W. Glass, who has resigned, and in addition to Edward Hinks (December 30th, 1936).

Ministry of Health

BACTERIOLOGICAL TESTS FOR GRADED MILK*

STANDARDS.—1. The following bacteriological standards for graded milks are prescribed by the Milk (Special Designations) Order, 1936:

Tuberculin Tested Milk including *Tuberculin Tested Milk* (*Certified*): *Accredited Milk.*—The milk when tested in accordance with the prescribed method must not decolorise methylene blue within 4½ hours if the sample is taken at any time from the 1st May to the 31st October; or within 5½ hours if the sample is taken at any time from the 1st November to the 30th April. The milk also must not contain coliform bacillus in 1/100 millilitre.†

Tuberculin Tested Milk (*Pasteurised*).—The milk must not contain more than 30,000 bacteria per millilitre.

Pasteurised Milk.—The milk must not contain more than 100,000 bacteria per millilitre.

SAMPLING.—Pars. 2 and 3 and 5 deal with the collection of samples, and Par. 4 with sampling from churns.

TRANSPORT AND STORAGE OF SAMPLES.—Directions for Tuberculin Tested and Accredited Milks are given in Pars. 8 to 10 and for Pasteurised Milk and Tuberculin Tested Milk (Pasteurised) for the Plate Count Test in Par. 11.

TECHNIQUE OF THE TESTS.—Section A deals with the apparatus and technique of the Methylene Blue Test. Stress is laid upon the point that the reliability of the results of the test depends upon the strict observance of the directions given in the Memo. (Pars. 13–26). Standard methylene blue tablets must be used for the test. Traces of impurities normally present in methylene blue seriously affect the reliability of the test. It is essential, therefore, that only specially prepared standard methylene blue tablets should be used for this test. The names of manufacturers who supply such tablets may be obtained on application to the Ministry of Health.

The test tubes used must conform to the British Standard Specification 152/16, nominal 6″ × ⅝″, having an internal diameter of 13·5 ± 0·5 mm. and an etched mark indicating 10 ml. One-ml. pipettes, preferably conforming to specified dimensions, are to be used, and no pipette should have an error in delivery of more than ± 2 per cent.

The milk is to be regarded as decolorised when the whole column of milk is completely decolorised or is completely decolorised up to within 5 mm. of the surface.

Section B (Pars. 27 to 34) deals with the Apparatus and Technique for the Coliform Test for Tuberculin Tested and Accredited Milks. The milk is regarded as satisfactory if two out of three tubes are found to be free from acid plus gas after 48 hours' incubation at 37° C.

Section C describes the Plate Count Test for Tuberculin Tested Milk (Pasteurised) and for Pasteurised Milk (Pars. 35 to 45), and the final paragraph (46) states that the results of the three tests should be recorded on forms similar to those given in the Appendix to the Memorandum, and that the report should be sent to the Licensing Authority immediately on the completion of the examination.

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* *Memo.* 139/Food (Jan. 1937). For official use.

† It is not necessary that every sample should be submitted to both tests, and Licensing Authorities which require to have frequent tests made of samples of producers' milk may find it convenient to have most of the samples examined by the methylene blue test alone, reserving the coliform test for occasional use.

SALE OF FOODS AND DRUGS

EXTRACTS FROM THE ANNUAL REPORT FOR 1935–36 AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1935*

THE samples of foods and drugs analysed by Public Analysts in England and Wales during 1935 numbered 143,831 (an increase of 3248 on the previous year), and the number reported against was 7972, or a proportion of 5·5 per cent. against 5·3 for 1934 (ANALYST, 1935, 60, 821).

PRESERVATIVES.—Of a total of 422 contraventions of the Regulations, 207 related to sausages, mostly on account of no declaration of the presence of the allowed proportion of sulphur dioxide. Boron preservative was found in cream, milk, butter, sausages, potted meats, etc.; formaldehyde in milk and in 2 samples of tinned smoked salmon, and sulphur dioxide in barley, minced, potted and other meats, pepper and vinegar. One minced meat contained 1860 p.p.m. of sulphur dioxide.

MILK.—The number of samples examined (78,674) shows a marked increase over the previous year, and of these, 5798 (7·4 per cent.) were reported adulterated or not up to standard. Of the 1048 "appeal to cow" samples, 406 were below the presumptive standard. Convictions were obtained in respect of a milk containing 24·7 per cent. of added water and of 4 milks with 19·2 to 39·6 of added water. Twenty samples contained added colouring matter, 8 samples boron preservative, and 11 formaldehyde. Of the 27 samples of skimmed or separated milks reported against, one contained colouring matter, one was stated to be whole milk, but in most cases there was a deficiency in non-fatty solids. Legal proceedings were instituted in respect of most of the samples found to contain preservative, and in one case in which the sample contained 2 p.p.m. of formaldehyde the producer was fined £25 and £1 11s. 6d. costs. Twenty-one samples (of 1186) of condensed milk were deficient in milk-solids, were unfit for human consumption, or contained the equivalent of less milk than was indicated on the label. Three dried milks (of 186) were unsatisfactory owing to deficiency of milk fat or contamination with foreign matter. One sample consisted of starch.

CREAM.—Fifteen of 1971 samples of cream were reported against, and 8 were deficient in fat. One "thick cream" contained 20·25 per cent. of fat, and two samples of tinned cream, labelled "Pure Thick Cream, a highly concentrated and rich cream," contained 18·5 and 20 per cent. of fat respectively.

BUTTER AND MARGARINE.—Of 8001 samples of butter and 2774 of margarine, 64 of butter and 7 of margarine had an excess of water; 7 butters contained boron preservative; 10 consisted wholly or partly of margarine; 4 contained excess of free fatty acids, and one was mouldy and dirty, whilst 45 margarines infringed the labelling regulations and 2 contained excess of milk-fat.

LARD AND OTHER FATS.—As many as 40 of 2688 samples of lard had unfavourable reports, mostly for containing foreign fats or oils. Of the 512 suets, 41 were reported against; undeclared or excessive starchy matter was present in most, whilst 3 contained excess of water and 3 gave evidence of decomposition.

CHEESE.—There were 24 adverse reports on 1458 samples examined; 4 samples were contaminated with tin and 2 with lead.

BREAD AND FLOUR.—Only one bread (containing fungus) of 264 examined was reported against and 6 of 1351 flours, one, sold as self-raising flour, being plain flour.

JAM AND MARMALADE.—There were 126 adverse reports on 1624 samples; 40 jams contained excess of sulphur dioxide, and one was also contaminated with copper and was deficient in fruit. One sample was heavily contaminated with mould spores; a "home-made" marmalade was factory-made, and most of the remaining samples were deficient in fruit or soluble solids, or infringed the labelling regulations.

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* Published by H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3d. net.

VINEGAR.—Of 1949 samples examined, 148 were deficient in acetic acid, 10 contained preservative, 8 contained vinegar eel-worms, one was contaminated with mouse droppings, and one contained excessive lead. In others, artificial vinegar was present in samples sold as "Malt" or "Table" vinegars.

The vendor of a sample of "table" vinegar, which proved to be artificial vinegar and to be 46 per cent. deficient in acetic acid, was fined £5 and 10s. 6d. costs.

SPIRITS AND BEER.—In 57 samples of whiskey, 26 of gin, 24 of rum, and 5 of brandy (from a total of 1706), the spirit had been reduced more than 35° under proof. Seven of 425 samples of beer were adulterated; 2 contained excessive amounts of sulphur dioxide, 3 excessive arsenic. A sample of ale contained at least 0·0003 per cent. of phenol, and a milk stout containing 5 per cent. of milk-sugar was reported against, as its description containing the words "Pure Dairy Milk" was misleading.

MISCELLANEOUS ARTICLES OF FOOD.—The 32,000 samples examined covered a very wide range and included potted meat containing excess of water, or starchy matter, or sulphur dioxide, or boric acid; sausages deficient in meat; fish cakes containing no fish; several samples of tinned fish contaminated with tin, involving destruction of stocks. Copper was present in tomato soup and catsup; copper and tin in tomato purée; copper and zinc in aerated water; copper and iron in frozen lambs' tongues and livers; zinc in gravy browning, in the liquor of pickled cucumbers, and to the extent of 640 p.p.m. in black treacle. Barleys and rices contained talc or other facing material; a ground rice contained a large admixture of maize flour similar to hominy, and tapiocas were sold as sagos. Samples of cinnamon, dried herbs, etc. contained sand, and some samples of dried mint, ailanthus leaves; baking powders were deficient in available carbon dioxide. The word "cream" in cake and pastry descriptions was responsible for a number of adverse reports. A wine contained 0·3 per cent. of linseed oil and traces of paraffin, and a "Ruby Fancy Tawny Wine" was a flavoured and coloured sugar solution.

A few samples of sugar contained sand, one contained 1·5 per cent. of salt, and some contained excessive quantities of sulphur dioxide.

DRUGS.—Of 6188 samples of drugs, 353 were adulterated or not up to standard. Various halibut oils were deficient in halibut oil, 3 cod-liver oils did not satisfy the B.P. antimony trichloride test, and 2 samples of "Malt Halibut Liver Oil" caramels, labelled as containing vitamins *A* and *D*, showed no evidence of the presence of any vitamins. A sample of orange quinine wine contained 800 p.p.m. of benzoic acid and no wine, and another sample consisted of a solution of quinine salt, sweetened with sugar, coloured and flavoured. Zinc, boric, carbolic, calomel and mercury ointments were amongst the samples reported against. Sweet spirits of nitre samples were deficient in ethyl nitrite, and solutions of iodine were deficient in, or contained excess of iodine or potassium iodide, or both. Some iodine ointments were more than 90 per cent. deficient in iodine. Talc was reported in aspirin tablets, and arsenic in tartrated iron. D. G. H.

Home Office

Statutory Rules and Orders. 1936. No. 686

FACTORY AND WORKSHOP. NOTIFICATION OF DISEASES (MANGANESE POISONING)

THIS Order,* dated June 29th, 1936, made by the Secretary of State, extends the provisions of Section 73 of the Factory and Workshop Act, 1901 (1 Edw. 7, c. 22), to manganese poisoning. It came into force on August 1st, 1936.

British Standards Institution

BRITISH STANDARD SPECIFICATION

NO. 718—1936. NEW BRITISH STANDARD FOR DENSITY HYDROMETERS

THE Committee entrusted with the work came to the conclusion that any attempt to standardise hydrometers type by type would tend towards perpetuating a state of quite unnecessary confusion rather than towards achieving simplicity and uniformity. They were, therefore, driven to consider the whole question of hydrometers and hydrometry from first principles.

As a result, their activities were concentrated on providing a standard specification for density hydrometers and on compiling appropriate tables for use with such hydrometers.

The hydrometers are adjusted to indicate density—mass per unit volume—in grams per ml. at 20° C. The basis of the scale is thus entirely free from ambiguity and is expressed in universally recognised units. A wide choice of hydrometers is provided of varying range and accuracy and The National Physical Laboratory has made arrangements for testing hydrometers for conformity with the specification.

The hydrometers have been designed so that changes in reading due to changes in surface tension are as small as practicable. The surface tension for which each hydrometer shall be adjusted is specified and simple correction tables are given for use when the hydrometers are read in liquids having surface tensions different from those specified should the accuracy desired render the application of these corrections necessary. Temperature correction tables and tables for use in the measurement of liquid in bulk are also included in the specification.

Tables giving, over a temperature range, generally from 10° C. to 40° C., the density and composition of a number of liquids including sugar solutions, sodium chloride solutions, caustic soda solutions, sulphuric acid, hydrochloric acid and nitric acid are in course of preparation and will be published separately. The tables correlate density and percentage composition and so can be used not only in conjunction with the standard hydrometers, but also with any other method of determining density.

The Committee will willingly consider suggestions for the preparation of tables for other liquids of industrial importance, and every endeavour will be made to provide any table considered to be of use to industry.

Copies of this Specification (B.S.S. No. 718) may be obtained from the British Standards Institution, 28 Victoria Street, London, S.W.1. Price 3s. 6d. (3s. 8d. post free in Great Britain and Ireland, 3s. 10d. post free overseas).

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* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1d. net.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Fat and Phosphatide-content of Wheat Germ. B. Rewald. (*Chem. and Ind.*, 1936, **55**, 1002–1003.)—The phosphatide-content of wheat germ (which is higher than that of other parts of the kernel) is important in bread-making, since, after removal of the germ, phosphatides in small amounts are added to bring up the phosphorus-content of the treated flour to that of the original grain. Determinations of the fat and phosphatides were made by the following method, found applicable to other natural products, such as egg, soya bean and animal tissues:—The germ is extracted with petroleum spirit, which extracts most of the fat and all those phosphatides which are in the so-called "free" state, *i.e.* not combined with proteins or carbohydrates. The extraction is continued until no more fat or lipoid substance is obtained. After removal of the solvent, a pale yellow substance remains. This is Extract No. I. The residue is dried until free from solvent and re-extracted with a boiling mixture of 80 parts of benzene and 20 parts of alcohol until exhausted. Sometimes more than twenty extractions are necessary. The extract, after removal of the solvents, is dark brown and contains fat, phosphatides and other substances. This is Extract No. II. By adding acetone to Extract No. I (which contains only fat and phosphatides) the fat is dissolved, and the insoluble phosphatides are washed with acetone until free from fat. The fat recovered from solution is very pale in colour, contains 11·2 per cent. of free fatty acids, is easily purified and can be used as a high-grade oil for nutritive purposes. The precipitated phosphatides, consisting of lecithin and cephalin, are separated by means of cold methyl alcohol, in which only the lecithin is soluble. The isolated lecithin (which contains 3·53 per cent. of phosphorus) is of a pale yellow colour and crystalline; the cephalin (containing 4·24 per cent. of phosphorus) is of a darker colour and crystalline. Extract II is dissolved in benzene to separate carbohydrates, proteins, etc., which are not soluble in this solvent, and the solution is treated with acetone to precipitate phosphatides and separate the fat. The fat is a dark brown oil containing about 25 per cent. of free fatty acids. The phosphatide fraction of this extract is of a dark colour. To separate carbohydrates and other substances still present, the phosphatide fraction is brought into colloidal solution in water, and the solution is extracted with ether, which extracts the phosphatides, leaving the other substances in the aqueous layer. As before, the lecithin and cephalin are separated by means of methyl alcohol. The phosphorus-content of the lecithin fraction thus separated was 3·49 and that of the cephalin fraction 4·94. The isolated sugar was a polysaccharide which could not be crystallised and which reduced Fehling's solution only after hydrolysis. The results obtained were as follows:—Extract I:—oil, 6·7 per cent.; lecithin, 0·181 per cent.; cephalin, 0·042 per cent. Extract II:—oil, 0·85 per cent.; lecithin, 0·31 per cent.; cephalin, 0·073 per cent. The total amount of phosphatides in wheat germ is thus 0·606 per cent., of which 63 per cent. is "bound." Of the total phosphatides, 80 per cent. is of the lecithin type and 20 per cent. of the cephalin type. The total amount of fat extracted was 7·55 per cent., but it is noteworthy that only 6·7 per cent. was extractable by petroleum spirit. A. O. J.

Determination of the Maturity of Canned Peas. V. B. Bonney and S. C. Rowe. (*J. Assoc. Off. Agric. Chem.*, 1936, 19, 607–619.)—The peas employed in the experiments, after being graded, blanched in boiling water and washed in cold water, were canned in brine containing 15 lb. of salt and 25 lb. of sugar to 100 gall. of water. The results of the following tests are tabulated in correlation with the district of cultivation, grade, variety and state of maturity of the peas. (1) *Drained weight.*—The contents of a can are transferred to a dish, mixed with twice their volume of water and poured on to an 8-mesh screen of diameter 8 inches and spread evenly over the surface. The screen is tilted as far as is possible without disturbing the peas and is allowed to drain for 2 minutes. The surplus water is removed by wiping the under surface of the screen with a cloth, and the peas are then transferred to a tared dish and weighed. (2) *Number ruptured over 1/16th inch.*—In 100 drained peas the number having the skin broken open by internal pressure to such an extent as to separate the broken edges more than 1/16th in. is counted. (3) *Number sinking in brine of sp.gr.* 1·12 (68° F.).—A weighed amount of drained peas is poured into this standard brine in a vessel which ensures that the brine is a little over 4 in. deep, and that the floating peas form a single layer. After 15 seconds the floating peas are skimmed off, drained by the method already described, and weighed. The percentage weight sinking in the brine is calculated. (4) *Solids insoluble in alcohol.*—A portion of the sample of drained peas is ground in a food chopper and stirred until homogeneous, and 20 g. are weighed into a 600-ml. beaker. After 300 ml. of alcohol (80 per cent. by vol.) have been added, the beaker is covered and the contents are heated to boiling point, allowed to simmer for 30 minutes and then filtered by suction through a dry tared paper on a Buchner funnel. The residue on the paper is washed with 80 per cent. alcohol until the washings are clear and colourless. The filter, with the solid matter, is dried at 100° C. for 2 hours, then in a desiccator, and finally weighed. A study of 157 samples of Alaska peas and 159 samples comprising 8 sweet varieties of peas showed that the figure for alcohol-insoluble solids provides an excellent criterion of maturity. With the exception of one sample (which gave the figure 22·8) the alcohol-insoluble solids were below 22 per cent. in all samples of Alaska peas which were not fully mature. The corresponding figure for sweet varieties of peas was 19 per cent. No samples of Alaska peas which were not packed from mature peas were found with over 5 per cent. showing a 1/16th in. rupture. Similarly, no peas which were not packed from mature peas showed over 17 per cent. sinking in the standard brine. Sweet varieties of peas, even when mature, are not appreciably ruptured when canned, and, since their sp.gr. is less than that of Alaska peas, very few sink in the standard brine. The effect of varying the composition of the brine was not investigated. A. O. J.

Determination of the Maturity of Canned Stringless [Snap] Beans. S. C. Rowe and V. B. Bonney. (*J. Assoc. Off. Agric. Chem.*, 1936, 19, 620–628.)—Three degrees of maturity are defined, *viz.*:—(1) *Tender*: small or medium-sized pods which snap readily when bent, the seeds being undeveloped in the pod; (2) *Fairly tender*: large pods which snap when bent, the seeds being well developed but tender; (3) *Distinctly mature*: large pods, tough, leathery, rubbery or limp, which no longer snap when bent, the seeds being generally well developed but slightly shrivelled. The beans were sorted into various stages of maturity and, after the ends had been removed by hand, were cut into inch-lengths and blanched in boiling water. The cans were then filled as full as possible by hand, and the interstices were filled with factory brine (2 to 3 per cent. of salt). Preliminary experiments proved that the amount of tough fibrous material in the pods and the percentage of seeds present are of value as criteria of the state of maturity of the beans. The methods employed were as follows:—(1) *Drained weight.*—The contents of a can are mixed with twice their volume of water and poured on to an 8-mesh screen. For cans containing less than 3 lb. net weight an 8-inch screen is used; for larger cans a 12-inch screen. The drained weight is then determined as described in the previous abstract. (2) *Weight of seeds.*—The seeds from 150 g. of drained material are separated and weighed. (3) *Fibrous matter.*—The drained beans (100 g.) separated from the seeds are cut into half-inch lengths, pulped in a mortar, transferred to the metal cup of a malted milk mixer with 200 ml. of boiling water and boiled for exactly five minutes with 25 ml. of 50 per cent. sodium hydroxide solution after the addition of a small piece of paraffin wax. The mixture is then stirred for exactly 5 minutes by means of a malted-milk stirrer (capable of a no-load speed of at least 7200 rev. per min.), and is filtered by suction through a monel metal 30-mesh screen fitted into a Buchner funnel, the pulp being washed with a ¼-inch stream of boiling water until free from alkali and again with a stream of boiling water until the pulp is removed and the washings are clear. The residual fibre is dried for 2 hours at 100° C. and weighed. (4) *Solids insoluble in alcohol.*—The remainder of the drained material is treated as described in the previous abstract. The beans investigated were graded by expert graders into 4 grades, *viz.*: (i) fancy, (ii) extra-standard, (iii) standard and (iv) sub-standard. The maximum limit of fibrous matter for grade (iii) was 0·08 per cent. With a single exception, the maximum seed figure for grade (iii) was 6 per cent. The maximum weight of solids insoluble in alcohol for grade (iii) was 7 per cent., but this figure is not as diagnostic as the amounts of seed and fibre. Many of the samples regarded by the graders as sub-standard contained an excessive amount of "strings" (particularly the variety Kentucky Wonder), but, even where there was objectionable string development, the pods did not contain sufficient fibre to render the product unsatisfactory. Toughness of string was measured as follows:—A string is removed from the pod and one end is immediately fastened to a clamp weighing ¼ lb. The string is held in the fingers at a distance of ½ inch from the clamp, and the weight is gently lifted. If the string supports the weight for at least 5 seconds, it is regarded as a tough string. Examination of the majority of the 104 samples for tough strings indicated that there should not be more than one tough string for each 2 oz. of drained material. A. O. J.

Determination of Reducing Sugars by the Rosenthaler-Curli Method. Y. Volmar and S. Klein. (*J. Pharm. Chim.*, 1936, **24**, 400–409.)—Methods for the determination of reducing sugars which depend on the use of a cupro-potassium reagent, with determination either of the quantity of cupric hydroxide necessary to oxidise the sugar, or of the quantity of cuprous oxide formed, have the disadvantages that elaborate precautions must be taken to prevent the re-oxidation of the cuprous oxide, and that the reduction may proceed too far, giving a precipitate which is a mixture of cuprous oxide, cuprous hydroxide and copper. The method studied by the authors is that of Rosenthaler (*Z. anal. Chem.*, 1904, **43**, 282; Abst., ANALYST, 1904, **29**, 209), Lehmann (*Arch. Hyg.*, 1898, **30**, 274) and Curli (*Bull. della Industria delle Conserve Alimentari*, 1934, **9**, 100), depending on the reduction of alkalinity which occurs during the oxidation of sugars by a cupric salt. The reduction of alkalinity is due to the formation of acids by oxidation of the aldehyde group of the sugars, and the conversion of cupric hydroxide in the cupro-potassium complex by the acids into insoluble cuprous oxide or hydroxide. The diminution in each reaction is directly proportional to the quantity of sugar. The reagents used are: (*a*) a cupric solution, containing 69·28 g. of pure crystalline copper sulphate in 1 litre of solution; (*b*) a glycerin solution, prepared by mixing 4 parts of pure glycerin with 1 part of boiled distilled water (the authors used twice distilled glycerin, as pure commercial glycerin always gave high results, but if the glycerin solution is made up with 70 per cent. alcohol instead of water, the results are the same as those obtained with twice distilled glycerin if the quantity of sugar to be determined exceeds 0·04 g.); (*c*) an N-solution of sodium or potassium hydroxide; (*d*) an $N/2$-solution of sulphuric acid, standardised against solution (*c*); (*e*) an indicator sensitive to organic acids, such as a 0·1 per cent. solution of Congo red or haematin, a 0·2 per cent. solution of methyl red, or a fluorescent indicator, such as umbelliferone. The method is as follows:—Thirty ml. of solution (*a*), 20 ml. of solution (*b*), 40 ml. of solution (*c*) and 50 ml. of boiled distilled water are mixed in a flask, heated to boiling, and treated gradually with 25 ml. of the sugar solution, which must contain less than 1 per cent. of sugar. The boiling is continued for about 2 minutes, and 50 ml. of hot boiled distilled water are then added. After cooling, the volume is made up to 250 ml., and the cuprous oxide is allowed to settle. A volume of 125 ml. is filtered through paper or asbestos, and the excess of alkali is titrated. A blank was carried out when very dilute sugar solutions were used, 25 ml. of boiled distilled water being added instead of the sugar solution. The quantity of sugar (M) is given by $M = K(40 - n)$, where n is the number of ml. of $N/2$ acid solution used, and K is a constant. This method was tested on solutions of glucose and other hexoses and pentoses (arabinose, laevulose, galactose, and invert sugar) of varying strengths from 0·02 to 1 per cent., and the values for the diminution of alkalinity N ($= 40 - n$) were determined. Up to 0·5 per cent. the diminution of alkalinity is exactly proportional to the quantity of sugar, the value of K in the above equation being 1·23. With more concentrated solutions the results obtained are slightly too low. The method can be applied to the determination of sucrose (which must previously be inverted by boiling with a drop of hydrochloric acid, followed by careful neutralisation of the liquid), lactose, and maltose, proportionality being exact for solutions of strengths up to 0·5 per cent.; K for lactose is 1·8, and for maltose 2·2. E. M. P.

Determination of Neutral Esters in Fermentation Liquids. L. Espil and E. Peynaud. (*Bull. Soc. Chim.*, 1936, 5th Series, 3, 2324–2325.)—The method previously described (*id.*, 1935, 2, 682) is suitable for simple solutions of neutral esters, but with other products (*e.g.* wine) the ethereal extract of the esters is coloured, indicating the presence of other substances, extraction at *p*H 7 is incomplete even after long periods, and there is evidence of the presence of acid in the extract. Petroleum spirit (sp.gr. 0·650, b.p. 45° to 70° C.), however, gives with such samples extraction-curves which tend rapidly to a limiting value and are similar in shape to those obtained with ether and simple solutions. In practice the solvent is distilled in such a way that it is condensed in fine droplets which pass through the sample under examination, so removing the esters and subsequently falling into a lower vessel containing a standard solution of sodium hydroxide free from carbonate; saponification then occurs, the residual alkalinity being determined when extraction is complete. The operation is continuous, and 50 ml. of wine may be treated in about 10 hours. Volatile acids in the alkaline liquid may be determined by acidification and distillation, the sum of the malic, tartaric and citric acids being obtained by precipitation as barium salts in 70 per cent. alcohol, and manganimetric titration. Data for a red Burgundy (pasteurised in 1893, the year of vintage), St. Emilion (1914), Sauterne and Medoc types (1923 to 1934), and Quinsac (1936) are, in milli-equivalents per litre:—Total acidity, 81, 89, 89 to 104, and 90; volatile acidity, 29·4, 19·4, 16·9 to 20·0, and 11·2; neutral esters of volatile acids, 3·1, 2·0, 1·65 to 1·9 and 1·0; neutral esters of tartaric, malic and citric acids, 0·5, 0·65, 0·5 to 0·95 and 0; neutral esters of lactic and succinic acids, etc., 2·1, 1·25, 0·85 to 2·3 and 0·5; *p*H value, 3·94, 3·50, 2·94 to 3·20 and 3·60; alcohol, 15·1, 11·1, 9·4 to 13·2 and 10·6 per cent. by volume.

J. G.

Detection of Ferrocyanide Fining in Wines. L. Chauveau and A. Vasseur. (*Ann. Falsif.*, 1936, 29, 470–472.)—The following modification of Braun's reaction (formation of potassium isopurpurate) has been found specific for the detection of ferrocyanide fining in wines. Four to twenty ml. of the wine are evaporated nearly to dryness after being rendered alkaline by a slight excess of sodium hydroxide. The residue is dissolved in a little warm water, and placed in a 100-ml. Erlenmeyer flask, a crystal of tartaric acid is added, and a strip of sodium picrate paper is inserted and held by the cork. On warming the flask on a water-bath the presence of cyanogen compounds is disclosed by the paper becoming orange-red in less than 20 minutes. Three hundredths of a mg. of hydrocyanic acid in a sample of 20 ml. may thus be detected. No advantage is gained by taking a larger sample of wine. The last traces of Prussian blue are precipitated very slowly from wines treated with ferrocyanide, and the deposit should always be examined by decomposing it with soda and treating it as described above. A positive reaction may then be obtained, even when the supernatant liquid has given a negative one. Also, a turbid sample of well-shaken wine may be tested, and ferrocyanide then detected in wines containing an appreciable amount of iron.

D. G. H.

Occurrence and Possible Significance of some of the Minor Component Acids of Cow Milk Fat. T. P. Hilditch and H. Paul. (*Biochem. J.*, 1936, 30, 1905–1914.)—Detailed analyses were made of the component acids of typical cows' milk fat, and the results were calculated (*a*) on the assumption that no unsaturated acids having a molecular weight lower than that of oleic acid were present, and (*b*) allowing for the presence of decenoic, tetra- and hexa-decenoic acids on the basis of special analyses made to determine the saturated ester-contents of the ester fractions which were obtained by the fractional distillation of the "liquid" methyl esters. When these results were compared with those obtained by the similar analysis of the component acids of the completely hydrogenated butter, it was found that the total amounts of the C_{16} and C_{18} acids present agreed only when the allowance was made, as in (*b*), for the presence of lower unsaturated acids. In addition to the traces of decenoic acid and about 1 per cent. of tetradecenoic acid which was reported by Bosworth and Brown (*J. Biol. Chem.*, 1933, 103, 115), the authors conclude that about 4 to 5 per cent. of hexa-decenoic acid must also be present. When this correction was applied, the amount of palmitic acid was increased by about 2 per cent., and the amount of oleic acid was reduced by about 5 per cent. No unsaturated acid having a molecular weight lower than that of $\Delta^{9:10}$ decenoic acid was detected, and the position of the double bond relative to the carboxyl group was found to be the same in the decenoic, tetra-, hexa-, and octa-decenoic acids of the butter-fat. It is suggested that these observations are in agreement with the hypothesis, put forward in earlier communications, that the lower saturated glycerides of milk-fats have been produced from pre-formed oleo-glycerides, and that these minor, lower unsaturated components may represent degradation products of oleo-glycerides which have escaped complete saturation to lower saturated groups. S. G. S.

Higher Saturated Fatty Acids of Butter-fat. G. E. Helz and A. W. Bosworth. (*J. Biol. Chem.*, 1936, 116, 203–208.)—Hexacosanoic (cerotic) acid has been isolated from butter-fat. This acid, which crystallises from acetone as nacreous plates, has m.p. 80·5° C., and forms a methyl ester which distils at 286° C. at 15 ± 0·1 mm. pressure and at 261° C. at 5 ± 0·1 mm. pressure. The m.p. of the methyl ester is 62° C., and that of the amide is 105–107° C. In the butter investigated a saturated fatty acid having a molecular weight higher than that of stearic acid was found and the available evidence suggests that this is hexacosanoic acid. S. G. S.

Presence of Hydrocarbons in Arachis Oil. H. Marcelet. (*Bull. Soc. Chim.*, 1936, [5], 3, 2055–2057.)—An investigation similar to that on olive oil (ANALYST, 1936, 61, 488, 772). The residue from the deodorisation process contained a large proportion of mechanically entrained oil and, when freed from water, showed practically the same properties, with the exceptions of acidity and unsaponifiable matter, as did the oil itself. The unsaponifiable matter was somewhat sticky, and on crystallisation from alcohol yielded large crystals which showed the characteristics of phytosterol, and an oily, coloured liquid. The isolation of this oil was accomplished by distilling under vacuum the residue from the refining of the arachis oil, followed by saponification of the distillate and washing with petroleum spirit. The amber-coloured, unpleasant smelling oil had a sp.gr. 0·8020 at 19° C. and n_D^{19} 1·4518. This oil was separated by distillation under a pressure of 3 mm. of mercury into three fractions, the first of which was too small in quantity for examination; the second and third fractions had the properties shown in the table.

	Fraction II	Fraction III
Boiling-point at 3 mm. pressure, °C. ..	120–125	180–185
Sp.gr. at 15°/15° C.	0·8200	0·8550
n_D^{19}	1·4650	1·4761
Iodine value (Hanus)	121	78
Molecular weight (by cryoscopic method)	209	267

Elementary analysis

		C	H
Fraction II. $C_{15}H_{30}$	Found	C 86·06	H 14·40
	Theoretical	C 85·71	H 14·28
	Theoretical molecular weight 210.		
Fraction III. $C_{19}H_{38}$	Found	C 85·52	H 14·45
	Theoretical	C 85·71	H 14·28
	Theoretical molecular weight 266.		

These two hydrocarbons are related to hypogaeic and arachidic acids and have been named "hypogene" and "arachidene" respectively. E. M. P.

Shea Nuts from the Gold Coast. (*Bull. Imp. Inst.*, 1936, **34**, 437–448.)—The present investigation follows previous work inaugurated to determine whether any definite varieties of Shea trees exist in Nigeria and the Gold Coast, and whether there are any differences in yield and quality of the fat obtained from individual trees (*Bull Imp. Inst.*, 1930, **28**, 123; 1931, **29**, 407; 1933, **31**, 334). Results are now tabulated of the examination of a further series of 21 samples of nuts from the same trees on the Yendi Shea Reserve from which previous samples were taken (*Bull. Imp. Inst.*, 1932, **30**, 282). The trees were selected to represent as great a range of variation as possible, especially in bark formation and leaf shape, and a description of each of the 21 samples of nuts and kernels is given. The percentage of moisture in the kernels varied from 6·7 to 13·4, with an average of 7·9 per cent. The kernels as received contained 42·6 to 52·7 per cent. of oil, with an average of 48·7; or 47·1 to 56·9, with an average of 53·1 on the moisture-free kernels. The oils contained 3·6 to 8·3 per cent. of unsaponifiable matter with an average of 4·9 per cent. The results, together with those previously obtained, indicate that the oil-content of nuts from a particular tree is liable to vary from year to year, as does also the proportion of contained unsaponifiable matter. The provisional conclusion drawn from the results of the examination of the previous series of samples, and also from Nigerian samples, namely, that the lower the proportion of oil in the kernel the higher the percentage of contained unsaponifiable matter, receives still further support. D. G. H.

Some Ray-liver Oils. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 397B.)—The liver oils of 5 members of the family *Rajidae* (skates) caught off Northern Japan have been examined. The proportion of oil in the livers varied between 30 and 61 per cent., and the oils were yellow or orange-yellow liquids, giving slight blue colours with antimony trichloride. The unsaponifiable matter from each oil was a yellow or orange-yellow crystalline mass of comparatively high m.p. and consisting mainly of cholesterol. The oils tabulated below were from the following species:—*Raja kenojei* (1*a*) and (1*b*); *R. porosa* (2); *R. smirnovi*, (3); *R. karagea*, (4); and *R. isotrachys*, (5).

Oils	(1*a*)	(1*b*)	(2)	(3)	(4)	(5)
Sp.gr. at 15/4° C.	0·9315	0·9359	0·9325	0·9310	0·9270	0·9195
n_D^{20}	1·4839	1·4870	1·4840	1·4825	1·4810	1·4750
Saponification value	184·3	183·3	183·5	181·4	180·9	176·5
Iodine value (Wijs)	203·5	235·0	203·2	190·1	176·8	130·9
Acid value	0·61	1·56	0·10	1·51	0·69	0·27
Unsaponifiable matter, per cent.	1·28	1·57	2·25	2·32	3·63	3·60
Fatty acids						
M.p. ° C.	29–30	32–33	27–28	30–31	27–28	clear at 25–26
Neutralisation value	192·1	190·0	194·1	193·0	195·5	188·3
Iodine value	210·8	240·2	209·1	194·7	185·3	132·6
Ether-insol. bromides, per cent.	70·7	89·0	72·0	67·2	55·4	28·2

D. G. H.

Liver Oils of some Deep Sea Fish. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1936, 39, 397–398B.)—The four fishes whose liver oils were examined were caught at 400 to 500 fathoms depth off North Japan, and comprised one member of the *Gadidae* family, *Antimora rostrata* Gunther (*a*), and three members of the *Macruridae*, grenadiers or rat tails, *Coelorhynchus productus* Gilbert and Hubbs (*b*), *Macrurus fasciatus* Gunther (*c*), and *M. armatus* Hector (*d*). *Antimora* yielded 52·9 per cent. of liver oil, *Coelorhynchus* 32·9, and *Macrurus armatus* 32·3 per cent. The following values were obtained for the oils:

Liver oils	(*a*)	(*b*)	(*c*)	(*d*)
Sp.gr. at 15/4° C.	0·9151	0·9266	0·9201	0·9168
n_D^{20}	1·4736	1·4792	1·4784	1·4739
Saponification value	171·8	182·8	173·9	174·0
Iodine value (Wijs)	112·8	169·3	136·7	116·8
Acid value	0·58	1·09	4·76	0·53
Unsaponifiable matter, per cent.	2·68	0·95	4·57	1·31
Fatty acids				
M.p.	liquid at 15° C.	clear at 30° C.	14–15° C.	15° C.
Neutralisation value	183·9	192·4	185·7	185·6
Iodine value	117·2	175·0	129·9	120·4
Ether-insoluble bromides, per cent.	17·8	50·6	27·2	19·1

With antimony trichloride the blue colours given by (*a*), (*b*) and (*d*) were far inferior to those obtained with cod-liver oil. The solid constituents of the crystalline orange-yellow unsaponifiable matter in each oil consisted mainly of cholesterol. The fatty acids of (*a*) and (*d*) were converted into the methyl esters and fractionally distilled, and the results showed that the component acids were mostly of the C_{18}, C_{20}, C_{22}, and C_{24} groups. Palmitic acid was present only in small amount, probably accounting for the low m.p. of the fatty acids. D. G. H.

Colouring of Cheese Crusts. J. Pien. (*Ann. Falsif.*, 1936, 29, 472–483.)—For cheese of Dutch type practically the only effective colouring matter that can be used in France under the present regulations is alkanet, and the present study aims at showing that in every way Sudan IV would be more suitable. From the point of view of technique it is exceedingly difficult to get extracts of alkanet of similar colouring capacities. Further, since alkanet is red in acid and blue in alkaline medium, and the cheese at the moment when it is covered by the red paraffin wax is slightly alkaline, it follows that in time there will be a change of colour towards violet. If fermentation occurs under the paraffin layer (and this will happen if the paraffin wax is applied at too low a temperature), this change in colour will begin in a few days. On the other hand, if the temperature of the paraffin wax is too high, an immediate colour-change occurs in the alkanet to dark violet. Sudan IV is not affected by the alkalinity of the crust, the colour remains entirely in the paraffin layer, and no discoloration of the cheese itself occurs. Sudan IV is quite safe to use, for a solution of the dyestuff in butter was fed as the only food to rats for several days, with no ill effects of any sort. Moreover, it is used in other countries for colouring the outside layer of cheese of the Dutch type. D. G. H.

New Differential Colour Reactions of the Cardiotonic Glucosides: Digitoxin, Strophanthin K, Ouabain and German Digitalin. J. A. Sanchez. (*J. Pharm. Chim.*, 1936, **12**, 549–558.)—These cardiotonic glucosides can be detected and distinguished from one another by colour reactions. The following reagents are required:—(*a*) Vanillin in hydrochloric acid; this is prepared by dissolving 0·30 g. of pure vanillin in 100 ml. of conc. hydrochloric acid, free from iron. (*b*) *p*-Dimethylaminobenzaldehyde reagent; four drops of sulphuric acid (sp.gr. 1·83) are added to a solution of 0·10 g. of *p*-dimethylaminobenzaldehyde in 20 ml. of 95 per cent. alcohol. (*c*) Bromo-sulphuric acid reagent; one drop of saturated bromine water is added to 20 ml. of sulphuric acid. *Methods.*—Either the crystalline glucoside or the official 0·1 per cent. pharmaceutical solution is used. With the former, the procedure is as follows:—*Digitoxin*: A fraction of a milligram dissolved in two drops of acetic acid is warmed for three minutes with 10 drops of reagent (*a*), in a test-tube in a boiling water-bath. The reddish colour first formed changes afterwards to an indigo-blue which is permanent. On addition of 1 to 2 ml. of acetic acid the colour is unchanged. *Strophanthin K*: A few milligrams in 2 drops of acetic acid are examined by the method described above. At the end of three minutes a deep blue turbid liquid is obtained; this becomes clear after the addition of acetic acid; the colour is not permanent. *Ouabain*: A fraction of a milligram is evaporated to dryness with 1 ml. of (*b*), in a porcelain dish on a water-bath. A very characteristic violet colour is obtained on acidifying with a few drops of acetic acid. *German digitalin* (digitalinum verum): Quantities of the order of 0·1 mg. are examined. The solid, mixed with 1 ml. of (*b*), is evaporated to dryness on a boiling water-bath. As the solvent evaporates, a series of zones of red colour is observed. The residue is dissolved in 20 drops of acetic acid, and a liquid miscible with water is obtained. This has a deep red, stable colour, like that of eosin.

As the glycerin and alcohol in the official solutions interfere with the colour reactions, they must be eliminated before the tests are applied. The methods of elimination are described. From digitoxin solutions, the solid is obtained for examination, while, from solutions of ouabain and German digitalin, aglucones are obtained as products of hydrolysis. The colour reactions of ouabain and German digitalin are due to the agluconic nuclei in their molecules. The colour reaction of

German digitalin is also given by digitoxin. These compounds may be distinguished from one another by treatment with (*c*), which gives a cherry-red colour with German digitalin, but no colour with digitoxin. E. B. D.

Alkaloid of *Equisetum palustre*. E. Glet, J. Gutschmidt and P. Glet. (*Hoppe Seyler's Z. phys. Chem.*, 1936, **244**, 229–234.)—An alkaloid and a hydrocarbon have been obtained from *Equisetum palustre*. The hydrocarbon had the formula $C_{21}H_{42}$, and was slightly soluble in chloroform, glacial acetic acid, alcohol and ether, less soluble in ethyl acetate or dilute acetic acid, and almost insoluble in water or dilute mineral acids. The alkaloid, which has been named "palustrin," had the formula $C_{12}H_{24}N_2O_2$. It was very soluble in water, slightly soluble in chloroform and ethyl acetate, less soluble in ether, and only difficultly soluble in benzene and petroleum spirit. The hydrochloride of the alkaloid crystallises in long white needles or rectangular cubes, having m.p. 181° C. The pharmacological action and the chemical constitution of this new alkaloid are being investigated. S. G. S.

Examination of *Phosphas Natricus Acidus*. M. P. H. Sitsen. (*Pharm. Weekblad*, 1936, **73**, 1575–1576.)—According to the *Codex Med. Nederl.* a solution of 138 mg. of sodium acid phosphate in 10 ml. of water containing dimethyl yellow should require 19·8 to 20·2 ml. of 0·1 *N* alkali to produce a red colour. According to Kolthoff, however, ("Mass-analyse," Vol. II, p. 139) dimethyl yellow has a *p*H range of 2·9 to 4·0, and since a solution of the pure salt (sodium acid phosphate?) has a *p*H value of 4·4, the above method cannot be accurate. If, however, titration is carried out with 0·1 *N* sodium hydroxide solution, free from carbon dioxide, in the presence of thymolphthalein (*p*H range, 9·4 to 10·6, *cf.* Kolthoff, *loc. cit.*, p. 140), an accuracy of 0·5 to 1 per cent. is obtainable, and 10 ml. are required to convert the sodium acid phosphate into the diphosphate; a 0·05 *M* solution of the latter has *p*H 9·6. J. G.

Biochemical

Selective Adsorption of Enzymes by Cellulose. H. Tauber. (*J. Biol. Chem.*, 1936, **113**, 753–757.)—Cotton exerts a selective adsorption towards enzymes, and therefore the use of this material for the filtration of enzyme solutions should be avoided, since much of the active material is adsorbed. If such solutions require clarifying, a centrifuge should be used, or, alternatively, glass-wool or open-texture, "fast" filter-paper. Adsorption of enzymes by cotton may prove a useful property in selective concentration or in testing the purity of crystalline enzymes, for the enzyme is not contaminated, as it may be when other adsorbents (inorganic gels, tannins, etc.) are used. S. G. S.

Activation of Fat-Catalase by Heat. J. Bodnár and J. Bártfai (Baubach). (*Hoppe Seyler's Z. phys. Chem.*, 1936, **244**, 225–228.)—The decomposing action of the fat from the pig on hydrogen peroxide, and the activity of a cell-free solution of fat-catalase prepared from the same source, are increased considerably (to a maximum of 112 per cent.) by warming for 2 hours. The optimum temperature for this heat activation is, for summer fat, 31° C., for winter fat, 42° C., and for the solution of the fat-catalase 45° C. The heat activation, at least for the fat-catalase solution, cannot be explained on the basis of haemolysis.

S. G. S.

Studies on Carotenoids IV. The Carotenoid of *Genista tridentata*. K. Schön and B. Mesquita. (*Biochem. J.*, 1936, **30**, 1966–1969.)—The principal carotene of the flower of *G. tridentata* proved to be β-carotene, but a little α-carotene was present. Both of these, together with lutein, have been isolated in the crystalline state, and it is also probable that other carotenoids were present. Since xanthophyll is related, in chemical structure, to α-carotene, whereas the hydrocarbons present in this case belonged to the β-carotene series, it is suggested that lutein may be related *in vivo* to β-carotene and *in vitro* to α-carotene. Sitosterol and another sterol, not identified, were also isolated. S. G. S.

The Provitamin of Egg Sterols. A. Windaus and O. Stange. (*Hoppe Seyler's Z. phys. Chem.*, 1936, **244**, 218–220.)—Boer *et al.* (*Konink. Akad. Weten. Amsterdam, Proc.*, 1936, **39**) have stated that in a commercial cholesterol, from an unnamed source, they found some ergosterol and suggested adulteration. The authors report that they also have found ergosterol in samples of cholesterol from animal sources, in material which could not have been adulterated. In one experiment, cholesterol from dried Chinese egg-yolk contained 0·18 per cent. of the provitamin, as determined by ultra-violet absorption. A solution of this was adsorbed on a column of aluminium hydroxide and subsequently eluted with a mixture of petroleum spirit, benzene and methyl alcohol in the ratio of 250: 250: 1·2. From an original amount of 5 kg. worked up in 35-g. batches, 4·2 g. of cholesterol containing 19·4 per cent. of the provitamin was obtained. This was re-adsorbed on a smaller column and eluted, and a yield of 0·745 g. of cholesterol with a provitamin content of 81·4 per cent. was obtained. Another adsorption and elution gave 0·423 g. containing 100 per cent. of the provitamin. This product, after re-crystallisation from a methyl alcohol–ether mixture had m.p. 155° C. Further re-crystallisation raised the m.p. to that of ergosterol (163° C.). The acetate and the *m*-dinitro-benzoate of the new substance gave no depression when mixed melting-points with the corresponding esters of ergosterol were taken. Catalytic hydrogenation of the provitamin with hydrogen and palladium black gave an α-ergostenol which, when mixed with α-ergostenol from ergosterol caused no depression of the m.p. It is therefore claimed that the provitamin isolated from an animal source, in this case egg-yolk, is identical with ergosterol obtained from the usual vegetable sources. It is suggested that the ergosterol was derived from the food of the hens.

S. G. S.

Colorimetric Estimation of Urinary Oestrin. G. Pincus, G. Wheeler, G. Young and P. Zahl. (*J. Biol. Chem.*, 1936, **116**, 253–266.)—The various methods for colorimetric determination of urinary oestrin have been compared on the oestrone and oestriol fractions of human and rabbit urines. It was found that the phenolsulphonic method of Cohen and Marrian (*Biochem. J.*, **1934**, **28**, **1603**) gave reliable results for the oestriol content in human pregnancy urines of the

6th to 9th months of pregnancy, but for earlier stages high results were obtained, owing to the presence of inactive materials which gave coloured compounds under the conditions of the test. Oestrone fractions always contained these substances, and results were therefore always high. A rough correction was possible by assuming that the slope of the absorption curve at 580–600$m\mu$ was correlated with the amount of other substances interfering at 514$m\mu$, and making the appropriate allowance. The reacting material in rabbit urines consisted almost completely of physiologically inactive material. The phenolsulphonic acid test of Cartland *et al.* (*J. Biol. Chem.*, 1935, **109**, 213) was found difficult to use with impure extracts because cloudy solutions formed and the colour faded rapidly. The benzoyl chloride test of Görtz (*Biochem. Z.*, 1934, **273**, 396) was found capable of distinguishing oestrone and oestradiol from oestriol, giving a more intense colour with oestrone than with oestriol. With the oestrone fractions of human pregnancy urine this test gave results practically identical with those obtained by the phenolsulphonic acid test, but with rabbit urine extracts the results obtained by this method were double those obtained by the phenolsulphonic acid method. The David test for oestriol (*Acta brev. Neerland.*, 1934, **4**, 464) was found to be specific for the crystalline hormone, but could not be used for extracts because of the formation of cloudy solutions. S. G. S.

Bacteriological

Use of Micro-Organisms in Sugar Analysis. Quantitative Differentiation of Fructose and Mannose. T. F. Nicholson. (*Biochem. J.*, 1936, **30**, 1804–1806.)—*Gaffkya tetragena* (*Micrococcus tetragenus*) has been used for the separation of fructose and mannose present in dilute solutions. When the use of this organism was combined with that of *Proteus vulgaris* and *Monilia krusei* it was possible to analyse mixtures of glucose, fructose and mannose and to determine added fructose and mannose in blood and urine filtrates. The scheme of analysis for sugar mixtures published by Harding and Nicholson (*Biochem. J.*, 1933, **27**, 1082) has been modified to include the use of *G. tetragena* in the following manner:—

(*a*) Determine glucose, fructose and mannose by *M. krusei*.
(*b*) Determine galactose in the residual fluid from (*a*) by *Sacch. marxianus*.
(*c*) Determine glucose and fructose by *G. tetragena;* (*a*)—(*c*) = mannose.
(*d*) (In absence of galactose) determine glucose by *P. vulgaris;*
(*c*) — (*d*) = fructose.
(*e*) (In presence of galactose) determine fructose and mannose in residual fluid from (*d*) by *M. krusei;*
(*a*)—(*e*) = glucose, (*e*) — mannose = fructose or (*c*) — glucose=fructose.

S. G. S.

Agricultural

Determination of Rotenone. R. R. Le G. Worsley. (*J. Soc. Chem. Ind.*, 1936, **55**, 349–357T.)—The method adopted for the determination of rotenone has the same basis as previously described methods, *viz.* extraction with a solvent, formation of a rotenone–carbon tetrachloride complex, and purification of the mplex with alcohol, but several disadvantages have been overcome, and the percentage of rotenone obtained is higher. Percolation is carried out in one of three sizes of tubes—¾ in. diam. for 10 to 20 g. of material, 1 in. for 20 to 40 g., and 1½ in. for 40 to 100 g., each tube about 18 inches long. The three tubes slide inside other tubes, preferably of metal, permanently fixed in the water-jacket. The inner tubes are drawn out at their lower ends and pass through rubber stoppers to filter-flasks immersed in cold water. In the tapering ends of the two larger tubes are placed perforated Gooch crucible discs, on which rest discs of filter-paper with a wad of cotton-wool. By using this apparatus the time of extraction is reduced to between ¾ and 2½ hours, depending on the amount of root used. The most satisfactory solvent was found to be ethyl acetate. The use of decolorising charcoal (5 per cent. for derris and 10 per cent. for Mundelea), mixed with the powdered material before its extraction, results in a slight but definite increase in the purity of the rotenone and carbon tetrachloride complex. The root or Mundelea bark is cut up into small pieces, dried in the air for 1 to 2 weeks, ground in a high-speed disintegrator, and bottled. The samples then contain 3 to 7 per cent. of moisture, and the amount taken for extraction should yield about 1 g. of rotenone. After extraction a weighed amount of pure rotenone is added to the resins to bring the content to at least 40 per cent., and 1 g. is added even if the amount is already up to, or above 40 per cent. This is stirred into the heated resins, and the mixture is warmed until solution takes place and then left to crystallise overnight in a desiccator containing carbon tetrachloride. The crystals are broken up, filtered off, washed with solvent (carbon tetrachloride + rotenone) until no further colour is obtained, and dried for 6 hours at about 40° C., and the weight, multiplied by 0·719, gives the amount of crude rotenone. The purity of the crude carbon tetrachloride complex is, except for occasional samples, between 91 and 96 per cent., and the mean value, 94 per cent., may be assumed in approximate routine work. Determination of the purity of the complex by optical rotation gives results, on the average, 2·6 per cent. too high. The purity can be accurately determined by recovering the rotenone from the complex by triturating with absolute alcohol (5 ml. per g.) saturated with rotenone, leaving the mixture overnight in a desiccator containing some alcohol, and filtering off, washing with alcohol and drying at 100° C. The purity of the recovered rotenone is about 99·2 per cent. and can be checked by optical rotation in benzene solution. Six different samples of *Derris elliptica,* two each of *D. malaccensis,* one of *D. polyantha,* and two of *Mundelea suberosa* bark were examined in detail, and full results are tabulated for three samples. D. G. H.

Determination of Fumigants. VII. Determination of Sulphur Dioxide and Sulphur Trioxide from Burning Sulphur. O. F. Lubatti. (*J. Soc. Chem. Ind.*, 1936, **55**, 344T–346T.)—The paper describes a macro method for the determination of sulphur dioxide and sulphur trioxide and a micro method for the determination of sulphur dioxide in sulphur dioxide fumigant obtained by burning sulphur; the gas sample is collected in the evacuated flasks of Page's apparatus (*J. Soc. Chem. Ind.*, 1932, **51**, 369T; 1935, **54**, 421T), 1-litre flasks being used for the macro method and 20-ml. flasks for the micro method. The gases are absorbed in sodium hydroxide solution, glycerin being used as a stabiliser for the sodium sulphite formed. For the macro determination of sulphur dioxide the indirect iodimetric method of Kolthoff ("Volumetric Analysis," Vol. II, p. 399) is accurate but inconvenient. Two satisfactory methods are: (*a*) a modification of that due to Vincent and Richards (*J. Pharm. Chim.*, 1900, **10**, 482; 1902, **16**, 207), in which iodine is liberated in the solution containing sodium sulphite by the interaction of potassium iodide and potassium iodate after acidification, and (*b*) direct titration with iodine. For the first method the sampling-flask contains 50 ml. of 0·1 *N* sodium hydroxide solution with 5 per cent. of glycerin, and not more than 80 mg. of sulphur dioxide are absorbed. The liquid is neutralised with 0·1 *N* sulphuric acid to the end-point of methyl orange. Ten ml. of a 10 per cent. solution of potassium iodide are added, followed by 50 ml. of 0·05 *N* potassium iodate solution and 50 ml. of 0·2 *N* sulphuric acid. The iodine liberated is titrated with 0·05 *N* sodium thiosulphate solution, starch solution being used as an indicator. A blank test is made, and the quantity of sulphur dioxide is calculated by difference. For the concentrations involved there is no significant difference between the results given by the indirect iodimetric method, the potassium iodate method and direct titration. As iodine volatilises from aqueous solutions, even in the presence of potassium iodide, it is advisable to use an all-glass titration system, such as that described by the author (*J. Soc. Chem. Ind.*, 1935, **54**, 424T).

For the determination of sulphur dioxide and sulphur trioxide the sampling-flask is charged with 50 ml. of 0·1 *N* sodium hydroxide solution containing 5 per cent. of glycerin. After the gas sample has been collected the excess of alkali is titrated with 0·1 *N* hydrochloric acid to the end-point of methyl orange, a colour standard being used for comparison. The solution is diluted with 200 ml. of distilled water containing 5 per cent. of glycerin, and 30 ml. of 0·2 per cent. starch solution is added. The sulphite is titrated with 0·05 *N* iodine solution, delivered from a burette incorporated in an all-glass system. A positive correction of 1 per cent. should be introduced when the concentration of sulphur dioxide in the solution exceeds 0·04 per cent. by weight.

For the micro-determination of sulphur dioxide the sampling flask is charged with 2 ml. of 0·05 *N* sodium hydroxide solution containing 5 per cent. of glycerol. After the gas sample has been collected the excess of alkali is neutralised with 0·05 *N* hydrochloric acid, methyl orange being used as indicator; 0·5 ml. of 0·2 per cent. starch solution is added, and the sulphite is titrated with 0·01 *N* iodine solution delivered from a 5-ml. burette, graduated in 0·02 ml., incorporated in an all-glass system. The above-mentioned correction of 1 per cent. should be introduced. The quantity of sulphur trioxide absorbed is too small to be determined volumetrically. E. M. P.

Determination of Lactose in Mixed Feed. D. A. Magraw, L. E. Copeland and C. W. Sievert. (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 605–607.)—The method is a modification of that of Magraw and Sievert (*Ind. Eng. Chem. Anal. Ed.*, 1935, **7**, 106) and gives more accurate results. It involves the conversion of starch and sugars by means of animal diastase, thereby reducing the time required for subsequent fermentation. The sample (16·25 g. weighed to within 0·03 g.) is mixed in a 300-ml. flask with about 200 ml. of distilled water and digested on the water-bath for 30 minutes. When cold, the mixture is made up to 300 ml. and centrifuged. Of the supernatant liquid, 150 ml. are treated in a 200-ml. flask with 0·25 g. of animal diastase at 52 to 55° C. for 25 to 30 minutes, after which the flask is placed in boiling water for 15 minutes. When the flask has cooled, a further 0·25 g. of animal diastase is added, and the conversion and subsequent heating are repeated. The mixture is cooled to room temperature and, after the addition of 75 mg. of invertase-melibiase scales and 1·5 to 2 g. of bakers' yeast, the flask is plugged with sterile cotton-wool and fermentation is allowed to proceed at 26·5 to 30° C., with a permissible upper limit of 33° C., for 17 to 18 hours. The liquid is then cooled, made up to 200 ml., and centrifuged. Of the supernatant liquid, 190 ml. are concentrated by boiling to 25 or 50 ml., washed into a 100-ml. flask with hot water, treated with 10 ml. of saturated lead acetate solution, diluted to 100 ml. and centrifuged. To 50 ml. of the clear solution in a 100-ml. flask 2·5 ml. of a 5 per cent. solution of mercuric chloride are added, and the mixture is allowed to stand for 15 minutes with repeated shaking. After the addition of 5 ml. of 20 per cent. phosphotungstic acid solution, the liquid is made up to 100 ml. and filtered if necessary. Hydrogen sulphide is passed in, the precipitate is filtered off, and 50 ml. of the filtrate are boiled to remove hydrogen sulphide, the water lost being replaced. Lactose is then determined by the Munson and Walker method (*Assoc. Off. Agric. Chem., Methods of Analysis*, 1930 Edition, p. 379), a Jena fritted glass crucible (1G4) being recommended for filtration. After being thoroughly washed the precipitate of cuprous oxide is dissolved in 5 ml. of hot dilute nitric acid (1 + 1), 0·5 g. of urea is added (Lyle, *Ind. Eng. Chem. Anal. Ed.*, 1936, **8**, 200), and the solution is boiled for 2 minutes. Copper is determined by titration with standard sodium thiosulphate solution (19 g. of the crystallised salt per litre), and the corresponding amount of lactose is obtained from Walker and Munson's table (*loc. cit.* p. 514). The number of grams of material used in the final aliquot portion is given by

$$\frac{150}{(300-8)} \times \frac{190}{200} \times \frac{50}{100} \times \frac{50}{(100-1)} \times 16{\cdot}25 = 2{\cdot}00 \text{ grams}$$

a total correction of 9 ml. having been made for volumes of precipitates. The percentage of lactose in the original material is given by $\frac{(x - 0{\cdot}006)100}{0{\cdot}96 \times 2}$, where x = lactose determined, 0·006 is a correction for a blank determination, and 0·96 is a correction for loss of lactose during fermentation. Examples of determinations of known amounts of lactose added to feeding stuffs are given, and these show that the method gives accurate and consistent results. A. O. J.

Water Analysis

Photometric Determination of Silicate in Sea Water. R. J. Robinson and H. J. Spoor. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 455–457.)—The colorimetric method of Dienert and Wandenbulcke (*Compt. rend.*, 1923, **176**, 1478), various modifications of which have been proposed by different workers, has been investigated. The method, which involves colorimetric determination of the yellow silico-molybdate complex formed in the acidified silicate solution on the addition of ammonium molybdate, was studied by measuring the transmission of light through the coloured solution with the aid of a Zeiss Pulfrich photometer. It was found that the colour developed to full intensity within 3 minutes, and did not fade until at least 2 hours later. Temperature had no effect on the intensity of colour between 6° and 22° C. A repetition of the work of Swank and Mellon (*Ind. Eng. Chem., Anal. Ed.*, **1934**, **6**, 348) with fresh waters confirmed their findings that the Winkler reagent with hydrochloric acid (*Z. anorg. Chem.*, **1914**, **27**, 511) yielded 1·09 times as much colour for the same amount of silicate as the reagent of Dienert and Wandenbulcke with sulphuric acid. In synthetic sea water, the colour-intensity was essentially the same with either reagent. The maximum development of colour occurred between *p*H values of 1·5 and 2·3; with increased acidity, slightly less colour developed. Tests were made of the applicability of permanent colour standards of potassium chromate and sodium borate solution (Swank and Mellon) and picric acid (King and Lucas, *J. Amer. Chem. Soc.*, **1928**, **50**, 2395). The chromate standard was found for various reasons to be preferable. The applicability of Beer's law relating to variation in colour with dilution was studied by plotting the negative logarithm of the light transmission against silicate concentration. The law was found only to apply approximately with concentrations of silicate greater than 0·20 mg.-atomic proportions of silicon per litre, but it held satisfactorily at lower concentrations. For the same silicate concentration, less silicomolybdate colour developed in a sea-water medium than in fresh water, the ratio being 1 : 1·16. A correction factor according with this ratio is therefore required if permanent colour standards are used. S. G. C.

Organic

Study of the Resorcinol Reaction of Oxalic Acid. M. Pesez. (*Bull. Soc. Chim.*, 1936, [5], 3, 2072–2074.)—The colour reaction of oxalic acid with resorcinol previously described (*Bull. Soc. Chim.*, **1936**, [5], **3**, 676) has been modified as follows:—One ml. of cold sulphuric acid (1 : 2) is added to 5 ml. of the solution to be examined, followed by a few pieces of zinc-copper couple or 2 drops of a 10 per cent. aqueous solution of copper sulphate and about 1 g. of zinc. After about 3 minutes, 0·2 ml. of the reduced solution, which contains glyoxylic acid, is added to 2 ml. of conc. sulphuric acid (sp.gr. 1·84) in a test-tube, followed by 0·1 ml. of Denigès' resorcinol reagent (2 per cent. aqueous solution of resorcinol). A pale blue colour develops in the cold and becomes intensely blue on heating on a water-bath. The reaction is very sensitive and will detect 0·10 g. of oxalic acid in 1 litre of distilled water, or 0·02 mg. in the sample under examination; it can be carried out in the presence of hypochlorous, chloric, bromic, nitrous, nitric, and chromic ions. If hydrobromic or hydriodic ions are present, the procedure is modified as follows:—Two ml. of sulphuric acid are placed in a test-tube and mixed with 2 drops of the resorcinol reagent; 4 drops of the reduced solution are run down the side of the tube. In the presence of oxalic acid a blue ring forms at the junction between the liquids; in presence of tartaric acid and absence of oxalic acid a violet-rose ring forms.

This reaction invalidates the colour test for tartaric acid if oxalic acid is present. The following procedure is recommended for the elimination of the oxalic acid. Five ml. of the solution are treated with 3 to 4 drops of dilute sulphuric acid (1 : 2), followed by the gradual addition of calcium carbonate, with shaking, a slight excess of calcium carbonate being added. Glacial acetic acid is then added, drop by drop, until the odour persists (3 to 4 drops after the cessation of effervescence), and the liquid is treated with a few crystals of a neutral soluble sulphate (sodium, potassium or magnesium sulphate). After shaking, the liquid is filtered through a pleated paper, and the filtrate is treated with 1 ml. of sulphuric acid (1 : 2), 2 drops of a copper sulphate solution and a piece of zinc. After 2 to 3 minutes the reduction product is condensed on a water-bath with the resorcinol or bromoresorcinol reagent in conc. sulphuric acid, using 2 drops of solution and 2 drops of reagent in 2 ml. of acid. The rose-violet colour of the Molher-Denigès reaction or the blue colour of the author's reaction is then obtained in the presence of tartrates. E. M. P.

Determination of Semicarbazones. S. Veibel. (*J. Pharm. Chim.*, 1936, **24**, 499–502.)—The author's method (*Bull. Soc. Chim.*, 1927, [4,] **41–42**, 1410; Abst., ANALYST, 1928, **53**, 53) for the determination of semicarbazones is as follows:—A weighed amount of semicarbazone is boiled with sulphuric acid (10 to 30 per cent.) for ½ to 1 hour; the semicarbazone is hydrolysed with formation of aldehyde (or ketone), hydrazine, and ammonia. The hydrazine is removed by oxidation with iodic acid, the iodine formed is distilled off until the colour of the iodine has disappeared, and the ammonia is then determined in alkaline solution by the Kjeldahl process. This method is compared with that of Harlay (cf. *J. Pharm. Chim.*, 1936, **8**, 23, 199), which is based on the determination of hydrazine. The latter process is not satisfactory for the determination of semicarbazones of formaldehyde, cinnamic aldehyde and citral, nor for those of α-ketonic acids, owing to the formation of aldazines. Veibel's method is not satisfactory for the semicarbazone of formaldehyde, but is satisfactory for those of cinnamic aldehyde, of citral, and of pyruvic acid. The derivative from citral was a mixture of the α- and β-compounds; and results indicate that both α-citral and β-citral can be determined by this method. The following analytical results were obtained:

Semicarbazone of	Molecular weights	
	Found	Calculated
Cinnamic aldehyde	190·7	189·1
Citral (α- and β-)	210·1	209·2
Pyruvic acid	(*a*) 145·3	145·1
	(*b*) 144·9	

[The m.p. for the semicarbazone of pyruvic acid given by Beilstein is about 200° C. Veibel, with this compound re-crystallised, finds 220–222° C. by warming slowly and 246–248° C. with the Maquenne block.] E. B. D.

Relationship between Chemical Composition and Mechanical Strength in the Wood of English Ash (*Fraxinus excelsior*, Linn.). K. R. Bamford and E. D. van Rest. (*Biochem. J.*, 1936, **30**, 1849–1854.)—The percentage amount of Cross and Bevan cellulose increased in passing from the periphery towards the pith of ash wood. The percentage amounts of lignin and extractives tended to decrease in the same direction, while the furfural-yielding complexes remained virtually constant in amount throughout a cross-sectional disc of any one tree. It was also found that the Cross and Bevan cellulose of ash heartwood contained more hexosans and less furfural-yielding material than the corresponding component of the sapwood. The defect known commercially as "black-heart" was associated not with any irregularities in the proportions of the three major components present in the wood, but apparently with some minor constituent. Variations in the Cross and Bevan cellulose appeared to be the cause for the variations in crushing strength in pounds per square inch of wood substance. In the material examined, the specific gravity, the cellulose-content and the strength increased in a direction from the periphery towards the pith. S. G. S.

Scientific Examination of Handwritings in Country-made Carbon Inks. S. Dutt. (*Document Investigation*, 1936, 4, 3–6.)—The inks in question are used largely in India in rural districts, and, to a less extent, in towns. They are prepared by suspending the soot collected from smoky lamps or burning oil in a gum made from glue, gum arabic, or gum acacia, or from starch- or sugar-products, and as they are not preserved they decompose in time, becoming more black at first, although they become fainter with age, and may eventually be obliterated. This is due to the fact that the pigment does not penetrate below the surface of the paper to the extent of more than 10 per cent. of its thickness, and, although the gum may penetrate to the extent of 50 per cent. of the thickness, it is completely destroyed within 12 years by oxidation, especially in the presence of air and moisture. This destruction of the binding medium facilitates the removal of the carbon particles by handling, friction, or even contact with another sheet, and it may be demonstrated by the absence of any colour-reaction when a cross-section of the sheet is stained with a solution of phloroglucinol or α-naphthylamine in hydrochloric acid, or by differential staining with Herzberg's stain, osmic acid, safranine or Capri blue. If glue has been used, however, the application of a 10 per cent. solution of phosphomolybdic acid to the surface of the paper will reveal the original writing as a light green-brown stain. Lampblack from kerosene oil has the appearance under the microscope of thick, coarse, brown-black granular masses, and in plane-polarised light the tips of the granules glisten against a dark background. Turpentine oil or rosin yields a similar pigment which has a finer structure, whilst pigments from non-drying oils (*e.g.* castor oil, mahua oil and coconut oil) are still finer and have a glossy violet-black shade. Linseed, tung, groundnut, sesame or mustard oil and fish oils yield the most uniform and most permanent pigments, and these vary in colour from deep blue to jet black. Most of these pigments contain from 3 to 10 per cent. of the original oil, as well as characteristic resinous compounds, and in filtered ultra-violet light these fluoresce as follows:—Kerosene, bright violet or purple; turpentine, moderately intense green-brown; coconut, castor or mahua oil, dull orange-brown; sesame or groundnut oil, pale brown-yellow; linseed or tung oil, very faint green-yellow; fish oil, light purple-yellow. The fluorescence is rendered more easily visible if the paper is treated with a solvent (*e.g.* ether) and carefully dried, as this spreads the oil, but the fluorescence decreases in the course of time and disappears after 3 to 5 years if the inks were derived from kerosene, rosin or turpentine, 4 to 6 years for castor, mahua or coconut oil, and 6 to 8 years for the other oils. If fresh handwriting is placed in contact with a fast photographic plate (*e.g.* Ilford "Golden Isozenith") under pressure for 2 weeks in the dark and the plate is then developed in a slow-action, fine-grain metol developer and intensified if necessary, a positive image of the writing results. This is attributed to gases occluded by lampblack when it is formed or evolved as it oxidises, and this property of the ink decreases gradually in the course of time, disappearing in 3 years. This type of writing may be preserved and protected from forgery by immersing the document in a 2·5 per cent. solution of cellulose acetate in acetone for 10 minutes; the excess of liquid is drained off and the document is dried in the shade at room-temperature. The percentage composition of the 22·3 per cent. of solid matter contained in a typical ink was as follows:—Carbon, 77·9; gum, 6·8; oil or fat, 7·3; resinoids, 3·9; ash, 6·3 (contained large quantities of potassium carbonate and sodium chloride, with calcium, magnesium, aluminium, silicon, sulphate and phosphate, and traces of other metals). J. G.

Inorganic

Hexanitrato Ammonium Cerate as a Standard in Oxidimetry. G. F. Smith, V. R. Sullivan and G. Frank. (*Ind. Eng. Chem., Anal. Ed.*, 1936, 8, 449–450.)—Hexanitrato ammonium cerate $(NH_4)_2Ce(NO_3)_6$, is proposed as a standard material for preparing ceric salt solution for volumetric titration purposes. It is an anhydrous non-hygroscopic salt and may be readily prepared in a pure condition from thorium-free cerium oxide containing praseodymium, neodymium and lauthanum. The salt is easily soluble in dilute sulphuric acid, yielding a solution which is stable under ordinary conditions of storage and also on heating at 100° C. The nitrate ion in the salt was found to have no influence upon the accuracy in the determination of ferrous iron, and was not expected by the authors to interfere with various other determinations for which a ceric sulphate solution is normally employed. It is stated that standard solutions free from nitrate may be prepared, if necessary, by dissolving a known weight of hexanitrato ammonium cerate in sulphuric acid, removing nitric acid by heating, and dissolving the residue in water. The salt is available commercially. S. G. C.

Volumetric Determination of Mercury. N. H. Furman and H. M. State. (*Ind. Eng. Chem., Anal. Ed.*, 1936, 8, 467–468.)—The method of Spacu and Dick (*Z. anal. Chem.*, 1929, 76, 273), in which mercury is precipitated as mercuric pyridine dichromate, has been modified, the dichromate ion in the precipitate being determined volumetrically. To the mercuric chloride solution (140 ml.) 10 ml. of ammonium dichromate solution (20 per cent.) are added. The liquid is stirred vigorously while 1 ml. of pyridine is added. After standing for 10 minutes, the yellow precipitate is filtered off on a sintered glass filter, a solution containing 0·5 g. of ammonium dichromate and 0·5 ml. of pyridine per litre being used to transfer the precipitate to the filter. The precipitate is washed 6 to 8 times with acetone; air is finally drawn through the filter to cause evaporation of the acetone, and the filter is placed in a vacuum desiccator for 10 to 15 minutes. The precipitate is then dissolved in dilute acid, and the dichromate ion is titrated either iodimetrically or with ferrous sulphate solution. In test experiments 50 ml. of 1·2 *N* hydrochloric acid was used to dissolve the precipitate; the ferrous sulphate titration was carried out either potentiometrically or with diphenylamine as indicator. Results very close to the theoretical were obtained with 0·1443 to 0·2654 g. of mercuric chloride. S. G. C.

Analysis of Magnesium Alloys. W. H. Withey. (*J. Soc. Chem. Ind.*, 1936, **55**, 357–359T.)—*Calcium.*—The preferred method for magnesium-calcium alloys is as follows:—A 1 to 2-gram sample is dissolved in hydrochloric acid, and twice the amount of *N* sulphuric acid required to combine with the calcium is added. The solution is evaporated to dryness on a steam-bath; 50 to 70 ml. of industrial alcohol are added, the mixture is well stirred, and the calcium sulphate, which remains undissolved, is filtered off and washed with alcohol; the calcium is finally determined as oxide after one or more precipitations as oxalate. It was found in tests that, although the theoretical amount of sulphuric acid is enough to fix the calcium, twice the amount is advisable; a greater excess produces more magnesium sulphate than can be dissolved in the alcohol used. The method of precipitation of the calcium from the solution of the alloy by the addition of sufficient oxalic acid to combine with all the calcium and magnesium (precipitation at room temperature), followed by re-precipitation of the calcium oxalate to purify it, was found to lead to slight loss of calcium, to the extent indicated by the following results:

Oxalate method	Sulphate method
3·98 per cent.	4·03 per cent.
0·79 ,,	0·83 ,,
20·56 ,,	20·60 ,,

Cerium and other constituents.—A 1 to 1·5-gram sample of the alloy is dissolved in hydrochloric acid, and *N* sulphuric acid is added in amount equivalent to twice the amount of metals, other than magnesium, which are present. The solution is evaporated in a shallow wide-mouthed beaker on a steam-bath until all free hydrochloric acid is expelled. The residue is treated with 50 to 70 ml. of industrial alcohol, and the insoluble sulphates are filtered off after settling, and washed with alcohol. After gentle ignition, the precipitate is dissolved in 5 ml. of hydrochloric acid, a few drops of hydrogen peroxide are added, the solution is neutralised with ammonia, and 3 per cent. by volume of conc. hydrochloric acid is added. The rare earths are precipitated by addition of enough oxalic acid to provide an excess of 3 g. per 100 ml.; vigorous stirring of the solution, and allowing it to remain for several hours at 70° to 80° C. (then overnight at the ordinary temperature) are advised. The precipitate of oxalates is filtered off, washed with "dilute acid" and ignited to oxides. The filtrate, containing the calcium, is neutralised with ammonia to precipitate calcium oxalate, and the calcium is determined in the usual manner. The alcoholic filtrate from the insoluble sulphates is evaporated to dryness and the residue is treated with hydrochloric acid and potassium chlorate to destroy traces of organic matter. The residue is dissolved and ammonium chloride is added. The solution is neutralised, made just acid with acetic acid, 5 g. of ammonium acetate are added, and the cobalt is precipitated as sulphide at 80° to 90° C. The cobalt sulphide is filtered off, washed with a slightly acid solution of ammonium acetate saturated with hydrogen sulphide, and the precipitate is converted into cobalt sulphate for gravimetric determination. The filtrate is made alkaline and saturated with hydrogen sulphide to precipitate the manganese as sulphide; the precipitate is filtered off, washed, and dissolved in 1 : 5 hydrochloric acid saturated with hydrogen sulphide in order to recover traces of cobalt which are sometimes found at this stage. In the absence of iron and aluminium, the manganese may be determined by means of bismuthate or as sulphate. In the presence of iron or aluminium it is more convenient to precipitate these two with ammonia before precipitating cobalt with hydrogen sulphide. A separate determination of manganese may be made by means of potassium persulphate in dilute acid, but the complete elimination of cobalt is very difficult, and the method suggested has proved more satisfactory. Good results were obtained in test experiments with synthetic mixtures made to simulate magnesium alloys containing a few units per cent. of cerium, calcium, cobalt, manganese and aluminium.

S. G. C.

Detection and Determination of Minute Quantities of Zinc by Means of Diphenylthiocarbazone. H. Fischer and G. Leopoldi. (*Z. anal. Chem.*, **1936, 107, 241–269.**)—The green solution of the reagent in carbon tetrachloride, chloroform, or carbon disulphide, when shaken with an approximately neutral aqueous zinc solution, turns purple-red. All other metals, with the exception of cobalt, palladium, and bivalent tin, can be masked by means of thiosulphate. By oxidation of tin to the stannic state and the agency of cyanide, the interference of these three metals is likewise overcome; hence the zinc test is specific for that metal. The limit of sensitiveness is normally 1 to 2γ in 0·1 to 0·5 ml. of solution. For the lengthy and complicated working directions, reference should be made to the original paper.

W. R. S.

Determination of Lanthanum by means of 8-Hydroxyquinoline. T. I. Pirtea. (*Z. anal. Chem.*, 1936, **107**, 191–193.)—The nitrate solution (50 ml.) is heated nearly to boiling, and treated with 5 ml. of 2 *N* acetic acid and an excess of alcoholic 3 per cent. solution of the precipitant, followed by 10 per cent. ammonia, drop by drop, until its smell becomes pronounced. The yellow lanthanum precipitate is allowed to settle for an hour, collected on a porous glass crucible, washed with warm water, and dried at 130° C. to constant weight (La factor, 0·2433). Alternatively the precipitate may be dissolved in 2 *N* hydrochloric acid and titrated bromometrically (ANALYST, 1927, **52**, 431); 1 ml. of 0·1 *N* thiosulphate is equivalent to 0·001167 g. La. (*Sic* in original).

W. R. S.

Rapid Method for the Determination of Selenium in Sulphur. W. C. Hughes and H. N. Wilson. (*J. Soc. Chem. Ind.*, 1936, **55**, 359–360T.)—The method consists in oxidising the sulphur with nitric acid, removing the nitric acid by evaporation, and ultimately reducing the selenious acid to elemental selenium by means of potassium iodide in the presence of a protective colloid, yielding a coloured solution which can be matched with standards. A 5-gram sample of the finely-powdered sulphur (150-mesh) is added, a little at a time, to 100 ml. of 94 per cent. nitric acid (sp.gr. 1·50). The solution is evaporated until fumes of sulphur trioxide are given off. [In some samples asphaltic matter is present which offers difficulty in oxidation, and repeated evaporation with nitric acid may be necessary. If the solution still remains coloured on dilution, it is best to match the slight colour by adding caramel solution to the standards before reduction of the selenious acid.] The residue is diluted to 80–85 ml. with water, and the solution is filtered, if necessary, and cooled; 10 ml. of 10 per cent. potassium iodide solution and 1 ml. of 5 per cent. gum arabic solution are added, and the solution is heated at 55° to 60° C. for 15 minutes, and then cooled. One ml. of starch solution (0·2 per cent.) is added, and the blue colour due to the liberated iodine is discharged by the addition of a slight excess of sulphur dioxide solution. The colour of the solution is matched colorimetrically with standards as noted below. Standard selenium solution is prepared by dissolving 0·050 g. of selenium in a few ml. of nitric acid; the solution is evaporated to dryness on a water-bath, and the residue is dissolved in 1 to 2 ml. of nitric acid and diluted to 1 litre. Suitable volumes of this solution are diluted to 80–85 ml., 8 ml. of pure conc. sulphuric acid (equivalent to 5 g. of sulphur) are added, and the liquids are treated in the same way as the test solution, as described above. The limit of sensitiveness of the method is 0·02 mg. of selenium. Samples of seleniferous sulphur which were tested were found to contain 0·01 to 0·02 per cent. of selenium. Sicilian and Texan sulphur are free from selenium. S. G. C.

Colorimetric Determination of Small Quantities of Bromine in the Presence of a large Excess of Chlorine. P. Balatre. (*J. Pharm. Chim.*, 1936, **29**, 409–413.)—The methods of Denigès and Chelle (*Comptes rend.*, 1912, **155**, 721, 1010; Abst., ANALYST, 1912, **37**, 58; *Bull. Soc. Pharm. de Bordeaux*, 1917, **55**, 75) and of Swarts (*Bull. Acad. Belg.*, 1889, **17**, 359), modified by Hahn (*Compt. rend.*, 1933, **197**, 245; Abst., ANALYST, 1933, **58**, 567), proved unsuitable for the determination of bromine in blood. The method of Stenger and Kolthoff (*J. Amer. Chem. Soc.*, 1935, **57**, 831), depending on the conversion of phenol red into bromophenol blue was adopted. The reagents required are: (*a*) phenol red solution, containing phenol red (phenol-sulphonephthalein) 33 mg., $N/10$ sodium hydroxide solution 3 ml., and distilled water to 100 ml.; (*b*) buffer solution, containing N sodium hydroxide solution 500 ml., and N acetic acid, about 650 ml.; (*c*) indicator buffer solution, containing phenol red solution 25 ml., and buffer solution to 500 ml.; (*d*) $N/200$ chloramine solution (0·07 per cent. solution of the sodium salt of monochlorotoluene-*p*-sulphonamide); as this solution does not keep well, its titre should be checked by titration with iodine, and it should be renewed frequently; and (*e*) $N/10$ sodium thiosulphate solution. The method is as follows:—Into a 30-ml. beaker are measured 5 ml. of bromide solution (containing 0·005 to 0·01 mg. of bromine, or 0·0075 to 0·0149 mg. of potassium bromide) and 2 ml. of indicator buffer solution. Two ml. of $N/200$ chloramine solution are measured into a small tube, and poured in one lot into the beaker. The liquid is agitated, and, after 15 seconds, the reaction is stopped by the addition of 3 to 5 drops of thiosulphate solution. The liquid is poured into a 10-ml. graduated tube, the beaker is rinsed with a few drops of distilled water, and the liquid is made up to 10 ml. The colour is measured with a Pulfrich photometer, using a spectral filter S.57 (wave-length about 572$m\mu$). With a depth of 20 mm. the coefficient of extinction is 0·31 for 0·01 mg. of bromine (an absorption of 51 per cent. of the incident light). The intensity of the colour follows the Lambert-Beer law. Under such conditions the error is less than 5 per cent. If a Pulfrich photometer is not available, the colour can be compared with a range of standards. E. M. P.

Determination of Acetylene in Liquid Oxygen. L. M. Jolson, J. J. Strishevsky and A. B. Bergelson. (*Zavodskaya Laboratorya*, 1936, No. 8, 852–3.)—Five measured litres of liquid oxygen are gradually poured into a vessel containing a copper spiral tube through which compressed air is being blown. When the volume has been reduced to about 100 ml. the gas is transferred to a heat-insulated copper container from which the vaporised oxygen is blown through special wash-bottles each containing 25 g. of freshly precipitated mercuric iodide, 30 g. of potassium iodide, 100 ml. of water, and a fragment of alkali. The precipitate is filtered off, washed with distilled water until free from iodine, transferred to a 250-ml. conical flask and dissolved in boiling nitric acid (1 : 3). The solution is titrated with $N/100$ ammonium thiocyanate solution—

$$HgC_2 + 2HNO_3 = Hg(NO_3)_2 + H_2C_2$$

$$Hg(NO_3)_2 + 2NH_4CNS = Hg(CNS)_2 + 2NH_4NO_3$$

One ml. of $N/100$ ammonium thiocyanate corresponds to 0·00013 g. or 0·11023 ml. of acetylene. The analysis takes 40 to 45 minutes, and the results are accurate to 0·01 ml. of acetylene. S. P. S.

Microchemical

Microchemical Identification of Ephedrine and Ephetonine. G. A. W. J. O. E. Paris. (*Pharm. Weekblad*, 1936, **73**, 1526–1527.)—To the edge of a drop of the solution to be tested is added a fragment of solid potassium oxalate. The hydrochloride of natural ephedrine immediately deposits bundles of needles and prisms which usually form fan-shaped groups, whilst well-formed thin diamond-shaped crystals are produced rapidly by ephetonine (the hydrochloride of the racemic synthetic product). Photomicrographs are provided. Addition of a drop of solution of sodium vanadate to a drop of the test solution produces a fine microcrystalline precipitate (similar in appearance to calcium oxalate in *Rheum*), and quill-shaped crystals, which are sometimes deformed and frequently grouped, respectively. This latter reaction is the more difficult to carry out successfully.

J. G.

Micro and Semi-micro Determination of Sodium and Potassium. M. Hegedüs. (*Z. anal. Chem.*, 1936, **107**, 166–175.)—The macro method of Szebellédy and Schick (ANALYST, 1934, **59**, 502) has been modified for application on a smaller scale. The solution of the mixed alkali chlorides or sulphates* is evaporated to dryness with 2 ml. of hydriodic acid in a small round-bottomed silica dish. If the dry residue is slightly yellow (free iodine), it is moistened with alcohol and again dried by evaporation. The mixed iodides are heated for 20 to 60 minutes (according to quantity) at 120° to 130° C., and are kept over strong sulphuric acid until ready for separation. The solvent used is a mixture of *iso*butyl alcohol and ether (1 : 1·5) saturated with potassium iodide by 10 minutes' agitation with the finely-powdered pure salt. The prepared solvent, which contains 0·66 mg. of KI (equivalent to 0·19 mg. K_2O) per 10 ml., is stored in the dark in a coloured glass bottle.

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* Szebellédy and Schick found that 0·25 g. of alkali sulphates could be completely converted into iodides by a single evaporation with 2 ml. of pure hydriodic acid, the sulphuric acid being eliminated by reduction, thus, $H_2SO_4 + 2HI = SO_2 + I_2 + 2H_2O$.

If the mixed alkali iodides weigh a few cg., they are extracted three times with 10 ml. portions of solvent, with intervening solution of the residue in hot water and evaporation to dryness. Each 10 ml. of solvent is applied in 2-ml. portions, the salt being thoroughly ground, after each addition, by means of a small glass pestle, for 1½ minutes. When a 10-ml. portion has been added, the solution is left to settle for about two minutes, and decanted from the residue through a filter-paper. The contact between dish and pestle should not be interrupted while the liquid is being poured on the filter, and the lip of the dish must be wiped with a small piece of filter-paper, which is thrown on the filter.

On a micro scale, the extraction is conducted with three 3-ml. portions, each of which is added in portions of 1 ml. with an intervening trituration for 1½ minutes. Ether (2 ml.) is added to the extract prior to filtration with decantation.

The filtrate, containing the sodium, is received in a 50-ml. glass dish. A few drops of 0·01 *N* thiosulphate solution and a little ethyl alcohol are added to prevent separation of iodine, due to a possible peroxide-content of the ether. The filter containing the insoluble potassium iodide is washed once with ethyl alcohol, then thoroughly with hot water, the washings being returned to the dish with a drop of hydriodic acid, and evaporated to dryness on the water-bath. The dry residue is ready for another extraction.

For the determination of potassium and of sodium, the insoluble fraction is dissolved in hot water, and the solution is evaporated on a water-bath; the combined extracts also are evaporated to dryness, as described. The iodine in both fractions is determined as follows:—The aqueous solution of the salt is treated with chlorine water until colourless, the iodide being oxidised to iodate. The solution is boiled in a small flask with a little pumice for the expulsion of free chlorine. The cooled solution is treated with 1 ml. of *N* hydrochloric acid and an excess of potassium iodide, and the liberated iodine is titrated with 0·1 (or 0·01) *N* thiosulphate solution. The potassium result requires no correction, but a deduction must be made from the sodium value found, for Na_2O equivalent to the potassium iodide present in the prepared solvent. The iodine determined by titration is six times the quantity equivalent to the alkali metal. W. R. S.

Determination of very Small Amounts of Bromide. F. L. Hahn. (*Mikrochem.*, **1935**, **17**, 222-235.)—It is shown to be theoretically impossible to determine small amounts of bromide in the presence of excess of chloride by oxidation methods depending on the liberation of the bromine. Success may be accidentally obtained by the liberation of some bromine together with an amount of chlorine equivalent to the bromine left behind. The fluorescein test for bromide in the presence of chloride has been made quantitative. *Reagents.*—(i) *Fluorescein.*—Five g. of the purest fluorescein dissolved in 5 ml. of 0·1 *N* sodium hydroxide solution and diluted to a litre. (ii) *Buffer solution.*—Approximately *N* sodium hydroxide and acetic acid solutions mixed in equivalent amounts and $\frac{1}{9}$ to $\frac{1}{10}$ the amount of excess acetic acid to give *p*H 5·6 to 5·5. (iii) Solution of chloramine-T, 0·01–0·1 molar. (iv) A 5 per cent. solution of sodium hydroxide containing 0·5 per cent. of sodium thiosulphate. The reaction equation is as follows:

$$\underset{\text{fluorescein}}{RH_4} + \underset{\text{bromide}}{4Br'} + \underset{\text{chloramine}}{4AmCl} = \underset{\text{eosine}}{RBr_4} + \underset{\substack{\text{toluene}\\\text{sulphamide}}}{4AmH} + \underset{\text{chloride}}{4Cl'}$$

For the determination of amounts up to 2γ of bromine 3 drops of buffer, 1 drop of fluorescein, 1 drop (0·01 molar) of chloramine-T are added to the solution, and the reaction is stopped by means of solution (iv) after 1 to $1\frac{1}{2}$ minutes. As the determination must be carried out at a definite *p*H, strongly acid or alkaline solutions must be neutralised to methyl red, the colour of which is destroyed under the conditions of the determination. Ammonia interferes and must be removed by evaporation with alkali.

A second method of determination, rapid but less accurate, has been based on Heyrowsky's polarographic method, which itself, however, was not sensitive enough. A mercury-calomel electrode was found to be very sensitive to small amounts of bromide in potassium chloride solution. The *comparative electrode* used is a calomel electrode with lead to a potassium chloride-agar solution, and, when not in use, the lead is dipped in a potassium chloride solution of the same concentration. Two different procedures are described, of which the second is suited for extremely small volumes:—(i) *Liquid electrode.*—About 0·5 to 1 ml. of the test solution is put into a small test-tube through the bottom of which a platinum wire passes, and a few drops of pure mercury are added as electrode, then a drop of a phosphate buffer solution, *p*H about 6, followed by a drop of 0·01 *N* of mercurous perchlorate solution. (ii) *Wire electrode.*—An electrode can be constructed of metallic mercury and calomel in an intimate mixture which will change its potential with the bromide-content of potassium chloride solutions if a platinum wire is polarised in a concentrated sublimate solution. The wire can either be dipped in the test solution, or bent round and the drop placed in the bend. A number of determinations of bromide in concentrations varying from 0·05 to 2·0 per cent. gave results differing from the calculated amounts by 0·00 to 0·03 per cent. The method is capable of being made more accurate. J. W. M.

Note on the Determination of Iodine. B. F. Stimmel and D. R. McCullagh. (*J. Biol. Chem.*, 1936, **116**, 21–24.)—The method, first published in 1934 (*J. Biol. Chem.*, 1934, **107**, 35) has been modified for the micro-determination of iodine in thyroid tissue and blood. For the determination in thyroid tissue, the fresh material, weighing between 5 and 100 mg., is placed in a 70-ml. nickel crucible with 0·5 to 1·0 ml. of a saturated solution of potassium hydroxide. This is heated over a Bunsen flame until the tissue disintegrates and is evenly distributed throughout the hydroxide. The crucible is then placed in a furnace at 100° C., and during a period of about 30 minutes the temperature is raised to 400° C., after which the crucible is immediately removed. The fused mass is washed into a 50-ml. Claissen flask with not more than 25 ml. of water. The auxiliary tube of the flask is sealed off, and the side-tube is connected with a condenser, the lower end of which goes to the bottom of a 50-ml. extraction flask which contains just sufficient water to cover the end of the condenser tube, 0·2 ml. of a 3 per cent. solution of sulphuric acid and 0·2 ml. of a 10 per cent. solution of sodium bisulphite. To the contents of the Claissen flask are added quickly 2 ml. of a 50 per cent. solution of sulphuric acid, 1 drop of a 10 per cent. solution of ferric sulphate, and 2 ml. of a 3 per cent. solution of hydrogen peroxide. More acid is added if necessary in order to make the solution definitely acid, as indicated by the presence or absence of ferric hydroxide. A glass bead is added to prevent bumping. The flask is immediately closed with a stopper and dropping funnel, the outlet of which has been drawn to a point. The contents of the flask are boiled vigorously over a micro-burner, care being taken to avoid flooding the side-arm of the Claissen flask. One or two additional amounts of 2 ml. of the 3 per cent. hydrogen peroxide solution are added through the dropping funnel during the distillation, but heating is discontinued during these additions to avoid carrying hydrogen peroxide over with the distillate. The distillation is discontinued when the volume in the Claissen flask is reduced to about 5 ml., or when sulphates begin to crystallise on the side of the flask. The extraction flask is then placed on a wire-gauze having an asbestos centre, and the contents are boiled gently for 2 minutes to expel carbon dioxide and sulphur dioxide, a glass bead being used to prevent bumping. The solution is immediately made alkaline to litmus paper by the addition of a 10 per cent. solution of potassium hydroxide; this should not require more than 3 drops. The solution is then carefully boiled down to a volume of 5 or 6 ml.; 1 drop of methyl orange solution is added, and the solution is neutralised by the addition of a 3 per cent. solution of sulphuric acid. Two drops of the sulphuric acid are added in excess and 5 drops of bromine water, which should cause the solution upon shaking to turn yellow immediately. It is then boiled down very cautiously to about 2 ml. and cooled on ice. This should require between 3 and 5 minutes in order to remove completely the excess of bromine with the minimum loss of iodine. One drop of a 1 per cent. solution of starch and 2 drops of a 1 per cent. solution of potassium iodide are added, and the solution is titrated with a 0·001 *N* solution of sodium thiosulphate which is delivered from a 0·2 ml. pipette graduated to 0·001 ml.

In determining the amount of iodine in blood, 10 ml. of blood are boiled with 12 ml. of a saturated solution of potassium hydroxide in a 300-ml. nickel crucible until foaming ceases. This requires less than 10 minutes. The crucible is placed in a muffle furnace at 250° C. for 30 minutes. The temperature is then increased to 360° C. over a period of 30 minutes. It is allowed to remain at 360° C. for 10 minutes, after which the crucible is removed. Sufficient water is added to the fused mass to form a fluid paste, which is extracted once with 25 ml. of 95 per cent. ethyl alcohol and four times more with 10 ml. of the same solvent. The combined alcoholic extracts are placed in a 300-ml. nickel crucible with 0·5 ml. of a saturated solution of potassium hydroxide. The alcohol is evaporated on the steam-bath, the contents of the crucible are gently dried over a free flame, and the crucible is placed in a muffle-furnace at 385° C. for 15 minutes. The ash is then transferred to a 50-ml. Claissen flask, and the procedure described for thyroid tissue is followed. S. G. S.

The Copper Benzidine Reaction in the presence of Halogen Salts and Thiocyanates, and a new Test for Copper. L. Kuhberg. (*Mikrochem.*, **1936, 20,** 153–160.)—The theories of the copper-benzidine reaction are discussed. For the test to be successful on filter-paper the solutions must be added in the following order: first, the drop of the copper salt solution, then benzidine, and finally the thiocyanate or bromide solution; *o*-toluidine reacts similarly to benzidine. Acetone is the best solvent for the benzidine or *o*-toluidine. Thiocyanates and bromides are used preferably to iodides in the reaction, as iodides form coloured products with a number of cations, and further are too easily oxidised. The *limit of identification* for the benzidine test is 0·08γ copper in 1:16,700 dilution for bromides and 0·01γ copper in 1:1,333,000 dilution for thiocyanates. The *o*-toluidine reaction is even more sensitive. The reagent solution contains 0·1 g. *o*-toluidine and 0·5 g. ammonium thiocyanate in 5 ml. of acetone. Aqueous solutions are unsuitable, as the copper-toluidine complex is somewhat soluble in water. The order of adding the different participants in the reaction is unimportant. When the drops were added from a fine capillary on to filter-paper, first a drop of the toluidine-thiocyanate reagent, then a drop of the test solution, the *limit of identification* was 0·003γ and the *concentration limit* 1: 5,000,000. The following ions interfere: silver, univalent mercury, bi- and ter-valent iron, ter-valent thallium, quadri-valent cerium, ter-valent gold, chloroplatinic acid and large amounts of manganese. The interference of silver may be prevented by precipitating it as chloride before the reaction, while iron may be converted into the complex $[FeF_6]'''$ ion by the addition of alkali fluorides, and in that form is without action on toluidine, so that it is possible to detect as impurity 0·00016 per cent. of copper in iron salts. In the presence of manganese a comparison test should be carried out on a saturated solution of manganese sulphate. In order to detect copper in the presence of the above-named oxidising agents and of univalent mercury, the differential reduction with liquid bismuth amalgam is applied, by adding 0·3 ml. of bismuth amalgam to 0·2–0·5 ml. of the test solution and then adding 3 to 4 drops of 0·5 *N* sulphuric acid. The micro-test-tube is shaken for 1 or 2 minutes, whereby $Tl^{\cdot\cdot\cdot}$ and $Ce^{\cdot\cdot\cdot\cdot}$ are reduced to $Tl^{\cdot}$ and $Ce^{\cdot\cdot\cdot}$, and $Au^{\cdot\cdot\cdot}$, $PtCl_6''$ and $Hg^{\cdot}$ are reduced to the metallic state. The mixture is filtered or centrifuged and 1 or 2 drops of a 10 per cent. iron ammonium alum solution are added to the filtrate; this completely converts the copper into the bivalent condition. Two or three drops of a saturated solution of sodium fluoride and sodium acetate are added, and the test is then carried out in the usual way. Bivalent tin should be converted to the quadrivalent form before the test. In this way copper may be detected in saturated solutions of the interfering cations.

J. W. M.

Physical Methods, Apparatus, etc.

Standard Liquids for the Microscopic Determination of Refractive Index. A. H. Kunz and J. Spulnik. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 485.)—The method of determination of refractive index which involves microscopic examination of a particle of the substance in a liquid of known refractive index (in which the particle is insoluble) requires a number of suitable liquids which differ in refractive index by small and regular intervals over the desired range (Chamont and Mason, *Handbook of Chemical Microscopy*, 1930). In view of difficulties in collecting such a set, from pure liquid compounds available, it is proposed to employ mixtures made up to definite values of refractive index as measured by a refractometer. It is desirable that the vapour-pressures of the constituents of a mixture should be nearly the same in order to ensure that the composition remains constant during use. Compounds in the undermentioned list have proved suitable.

Compound	Vapour Pressure mm.	Refractive Index/20° C.
α-Bromonaphthalene	3·5/110° C.	1·6582
n-Butyl phthalate	3·8/110° C.	1·4932
Heptylic acid	1·9/ 90° C.	1·4234
Mesitylene	27·15/ 20° C.	1·4981
Ethyl propionate	27·75/ 20° C.	1·3841

The range between 1·6582 and 1·4234 can be covered by mixtures of α-bromonaphthalene and heptylic acid, and the range between 1·4981 and 1·3841 by mixtures of mesitylene and ethyl propionate; *n*-butyl phthalate can be substituted for the more expensive heptylic acid above 1·4932. S. G. C.

Physico-Chemical (Conductivity) Method for the Determination of Chlorides in Biological Liquids. S. Mihaéloff. (*Bull. Soc. Chim.*, 1936, [5], **3**, 2395–2403.)—The liquid to be tested (0·05 to 1 ml.) is measured into the conductivity-vessel, and suitably diluted with water so that the electrodes are covered. The vessel is then warmed (by means of the hand) to a temperature 4° to 5° C. higher than that of the room, and it is maintained at this temperature (within 0·1° C.) by means of the hand during the titration (10 to 12 minutes); 0·5 *N* to 0·025 *N* silver nitrate solution is used, according to the amount of chloride present. The pipettes used for measuring the sample are made from glass capillary tubes having an internal cross-section about 0·1 square cm. in area, and they are calibrated by weighing the amounts of mercury which occupy given lengths; the pipetting error is reduced to 1 per cent. if traces of the sample remaining in the pipette are washed out with water, the washings being added to the sample in the cell. Special precautions to avoid errors due to evaporation are also described. Multiplicate determinations made on urine and defibrinated cow and sheep bloods showed that the mean error is less than 0·7 per cent. (corresponding with 0·1 g. of chloride ion per litre) when 0·1 or 0·2 ml. of solution is taken. Agreement with the Mohr, Volhard and persulphate methods was very satisfactory for the 7 urines tested, but the conductivity method gave the best reproducibility, besides being more rapid and requiring a smaller volume of sample. The mean chloride-contents found for whole blood, defibrinated blood and blood serum were 6·3, 6·6 and

6·0 g. per litre, respectively. Values (in g. per litre) for 15 individuals of either sex, aged 10 to 47 years, were 5·8 to 7·5 (mean 6·6) for serum, and 5·9 to 16·5 (mean 8·5) for urine. High results with both were obtained immediately after a meal, the greatest increases being 0·3 g. per litre for blood and 3·9 for urine. The importance of the ratio of the chloride-content of the urine to that of the blood as a measure of the retention of chlorides characteristic of certain haemo-renal disorders is emphasised, and it is maintained that this is preferable to the ratio of the corresponding electrical conductivities because it is a more sensitive indication and because the latter method is influenced also by the presence of mineral substances other than chlorides (*e.g.* sulphates and phosphates) in the blood; moreover, although the conductivity of serum is proportional to the chloride-content, this rule does not apply to urine. The method has also been adapted to the determination of inorganic conducting elements in cephalo-rachidian fluid. J. G.

Reviews

POISONS LAW. A GUIDE TO THE PROVISIONS OF THE PHARMACY AND POISONS ACTS, 1852 TO 1933, AND THE DANGEROUS DRUGS ACTS, 1920 TO 1932, FOR THE USE OF PHARMACISTS AND OTHERS CONCERNED WITH TRANSACTIONS IN DRUGS AND POISONS. By HUGH N. LINSTEAD. Pp. 444. London: The Pharmaceutical Press. 1936. Price 5s. net.

The law relating to poisons, always intricate, has become much more so since the introduction of the Poisons Act of 1933. Mr. H. N. Linstead, the able Secretary of the Pharmaceutical Society, has at the request of his Council written a book which does much towards reducing these intricacies to simple terms, and as a result he has produced a work indispensable to the pharmacist and to many others engaged in the distribution of poisonous substances. Although written primarily for the use of the pharmacist, it also contains information which concerns those engaged in the profession of analytical chemistry. The book includes chapters setting out in a precise form the powers and duties of the Pharmaceutical Society, the history of poison legislation and the responsibilities of the pharmacist; a perusal of these chapters may be commended to many correspondents whose letters printed in the ephemeral journals relating to chemistry have in the past shown much lack of understanding of these responsibilities.

In Mr. Linstead's book there is a skilfully written chapter describing the various ways in which the Rules and Regulations made under the Poisons and Dangerous Drugs Acts affect different interests. It includes the application of these Acts not only to pharmacists and others engaged in retail distribution, but also to wholesalers, manufacturers, medical practitioners, hospitals, educational institutions and laboratories, and this chapter sets forth most clearly under the separate headings those things which each may or may not do without offending.

The author has been fortunate in securing a remarkably clearly written chapter by Sir Malcolm Delevingne relating to the Dangerous Drugs Acts, and explaining with commendable lucidity the history of, and the case for, international co-operation in suppressing traffic in drugs of addiction.

Approximately one-half of the book—over 200 pages—is devoted to Appendixes. The first of these gives the text of the various Acts, and the various Rules, Regulations and Official Interpretations made under them, and the second gives a list of poisons and substances containing poisons included in the three Schedules to the Rules. The list is very full—it would be impossible for it to be exhaustive—and it gives in a form suitable for ready reference the proportions of poisons permitted in substances falling within the three Schedules.

Owing to the new Act, Rules and Regulations, it has become necessary for analysts to make accurate assays of various alkaloids, glucosides, etc., for which no well-authenticated methods of analysis exist; this need arises in order to determine whether certain preparations belong to Schedules 1, 2 or 3, according to the content of the poisonous substance. For example, preparations of gelsemium root containing 0·1 per cent. and upwards of alkaloid, or those of cantharidin containing 0·01 per cent. and upwards of cantharidin, are to be included in Schedule 1; consequently the accurate estimation of these substances in preparations containing amounts near to the permissible limit has become a matter to which the analyst has had to direct his attention since they came into force. The Analytical Methods Committee of this Society has lost no time in concentrating attention on this matter.

Finally, while the book is not to be regarded as a legal guide, it is an admirable and concise summary of the intricacies of poison legislation. FRANCIS H. CARR

FLAVOURS AND ESSENCES. A HANDBOOK OF FORMULAE. By M. H. GAZAN. Pp. 115. London: Chapman & Hall, Ltd. Price 25s. net.

This book contains over 300 formulae, prepared by a member of a Dutch family closely associated with the flavouring industry, and covers all the commoner fruit essences and many wine and liqueur flavours. The formulae consist mostly of compounds of natural essential oils mixed with various synthetic flavours—chiefly esters and aldehydes—and the author points out that "artificial flavours, however skilfully prepared, always lack the finish that characterises essences containing the natural fruit juice," so that he recommends the addition to the artificial essence of about 45 to 65 per cent. of natural fruit juice.

The formulae are divided into essences, "ethers," basic compounds, and extracts (from leaves, peel, root, etc.), and many of them are somewhat involved, owing to the numerous cross-references; for example, strawberry essence B contains proportions of six other essences, four of which are in turn composed of four or five other essences, and these are again compounded from others, so that to prepare any one essence one must have already prepared very many more. It is quite evident, therefore, that such formulae would be chiefly of value in large establishments where a great variety of essences are manufactured, though useful hints might be obtained by the chemist seeking to analyse or formulate a flavouring essence.

Formulae occupy 96 pages of the book, and the remaining 20 pages consist of an appendix giving a list, with properties, of the principal synthetic flavours, together with the usual methods for determining their specific gravity, boiling-point and melting-point, and also a note on colouring material. This appendix rather detracts from the character of the book, as there are many errors in the chemistry of the synthetics, and it might well have been omitted. Thus, acetaldehyde is said to boil at 122° C., benzoic acid to have a specific gravity of 122, sweet spirit of nitre to consist of ethyl *nitrate*, the formula of ethyl phenylacetate is given for phenyl ethyl acetate, and vanillin is said to be prepared by oxidising isoeugenol with alcoholic potash. In the section on colouring essences, details are given for the quantitative preparation of the concentrated dye solution, and of the quantities of the solution to be used in the various essences, but the nature of the dye itself is not even mentioned.

The book is well printed and attractively bound in leatherette, but its price appears rather high in proportion to its size and contents. W. H. SIMMONS

PREGL'S QUANTITATIVE ORGANIC MICRO-ANALYSIS. By HUBERT ROTH. Third English Edition, translated from the Fourth Revised and Enlarged German Edition by E. BERYL DAW, B.Sc., A.I.C. Pp. xvi + 271, with 72 illustrations. London: J. & A. Churchill, Ltd. 1936. Price 18s.

This is a very welcome translation of the only complete book written on the methods of organic micro-analysis, the German edition of which has already been reviewed in this Journal (ANALYST, 1936, 583). It is significant, as showing the enormous interest in micro-methods, that this work, first published in 1917, has been through four editions in German, and three in English since 1923. It is a model of what a textbook should be: it contains complete information, all of it thoroughly tested by experience, but it is a pity that the inadequacy of the index in the German edition could not have been remedied in the English edition.

The translator has done her work carefully and conscientiously. In her preface she states that she has "endeavoured to follow the original closely," and it might be objected that the result has been a translation that errs in being a trifle too literal. The book is well printed and is similar in format to the second English edition. JANET W. MATTHEWS

SEMI-MICRO QUALITATIVE ANALYSIS. By CARL J. ENGELDER, Ph.D., TOBIAS H. DUNKELBERGER, B.S., and WILLIAM J. SCHILLER, Ph.D. Pp. x + 265. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1936. Price 13s. 6d. net.

In this work the authors have aimed at applying the conventional methods of separation of the commoner inorganic ions on a semi-micro scale, making use of the technique of drop reactions. In this new technique the group separations and confirmatory tests are made upon about one ml. of the solution, and if this volume contains 1 mg. of each cation constituent and 5 mg. of the anion constituent, sufficient quantities are left after the separations to apply confirmatory tests, these being carried out on spot-plates or drop-reaction paper.

The book is divided into four parts. Part I (pp. 9–101) deals with fundamental principles of qualitative analysis, and discusses theories of ionisation, reaction velocity, mass action and many other subjects, including the theories of valency and the structure of atoms. Part II (pp. 102–177) gives a full account of the methods of separation and identification of the commoner cations. The group separations follow the well-established classical methods in macro-analysis, one notable change being the incorporation of the fairly recent method of Williams and

Briscoe (*Chem. News*, 1932, 145, 177) for the separation of calcium from barium and strontium. The underlying theoretical principles are well explained, and a comprehensive account of confirmatory tests for each cation is given, including numerous sensitive tests with organic reagents. In Part III (pp. 178–216), the reactions of the common anions are discussed, and in Part IV (pp. 217–246) a systematic scheme of micro-analysis is given.

The most welcome feature of the book, which will be of particular interest to analysts, is the inclusion of organic spot reagents for cations and anions. The authors have compiled an excellent up-to-date bibliography on the subject, comprising over five hundred references; but one cannot help feeling that some important reagents and tests in common use are either altogether omitted or very briefly mentioned. Thus on p. 121 the use of thiourea, which is a specific reagent for bismuth, is very briefly described, whereas considerable space is devoted to relatively unimportant tests, such as that with sodium stannite. Among some twenty reagents for copper (pp. 122–124), sodium diethyldithiocarbamate, introduced by Callan and Henderson, which is probably one of the most sensitive, is altogether omitted. The Gutzeit test for arsenic, in which, by the way, the authors use silver nitrate paper, is disposed of in eight lines, and no reference at all is made to the Marsh or Reinsch test. Again, all the authors have to say about thioglycollic acid, which is capable of detecting readily 1 part of iron in 5,000,000, is "thioglycollic acid gives a red coloration." An important point upon which the reviewer particularly wishes to lay stress is the necessity of giving *full* details of the interfering ions and the methods of eliminating them in the application of these tests. The use of spot tests has often found disfavour, owing to scant regard being paid to interfering substances. The benzidine test (p. 148) used for manganese is no more than a generic test for salts of a number of metals with oxidising properties.

Sufficient has been said to indicate that if there are to be, as we hope, further editions of this book, it would be useful to revise this subject critically and to give a few well-tried tests with full details of the technique and an adequate account of interference caused by other ions. As is frequently to be observed in similar books coming from America, the theoretical section seems far too long for a book on qualitative analysis. Some reference to theory is certainly an advantage and would, no doubt, be cordially welcomed by the student who wishes to have a thorough grasp of the subject, but inasmuch as a book of this kind is essentially practical, it would be better, perhaps, to keep the theoretical part within more reasonable bounds.

In fairness to the authors it must be said that the scheme which they here present, and which they have tested in teaching practice over a number of years, should commend itself to teachers because of the great economy of material and also because of the powers of observation developed in the pupil. Moreover, the professional analyst will find a wealth of information in the book; he should also derive from it numerous hints as to how to deal with the analysis of small amounts of substances, such as, for example, the ash of a food or drug, or a water residue. Those engaged in research in qualitative analysis in general, and in the use of organic reagents for inorganic analysis in particular, will find the book invaluable.

H. R. NANJI

Textbook of Applied Biochemistry. By F. C. Wokes, B.Sc., Ph.C., F.I.C. Pp. ix + 522, with 79 illustrations. London: Baillière, Tindall & Cox. 1937. Price 15s.

Sufficient of this book is devoted to descriptions of chemical and bio-chemical analyses, as well as to the theoretical considerations underlying those analyses, to make it of practical interest to readers of this journal, especially to those concerned with certain kinds of pharmacopoeial assay. Quite apart, however, from directly utilitarian value, it possesses special qualities that take it outside the ranks of the ordinary student's text-book. As a survey of modern bio-chemistry it has been so planned and written that it can be followed by all who have been taught chemistry—and have remembered most of what they have been taught. To chemists engaged in industrial or consulting practice—even to some engaged in research—if their work at any time involves contact with pharmaceutical manufacture or the examination of its products, Mr. Wokes has rendered a great service, even though his book was written primarily with the student in mind.

The chapter headings may be enumerated in substantiation of this claim, and not merely as a reviewer's method of padding. The author has with some originality begun by considering "The Biochemical Importance of Water." He then discusses in turn Hydrogen Ion Concentration; Surface Phenomena and Colloids; Spectroscopy; Sources and Properties of Ultra-Violet Light. There follow three chapters on Carbohydrates; Fats; Proteins and other Nitrogenous Compounds. The last four chapters are more pronouncedly biochemical, and contain admirable accounts of Enzymes and Respiration; Bacteria; Hormones; Vitamins. The book ends with an Appendix on International Biological Standards, a list of references and author-index, and a general index.

Any analyst who wants to fill up the gaps in his biochemical knowledge—whether those gaps have ever been filled before or not—will find the necessary material for most of them in this highly interesting and informative volume.

A. L. Bacharach

Survey of Imports, Raw Materials and Synthetic Products, and their Relationships to the Old and Newer Industries, with Special Reference to the Humber Area. A. R. Tankard. Pp. 54. The City Laboratories, Hull. Price 2s. 6d.

The City of Hull is to be congratulated upon this enlightened means of attracting new industries to its neighbourhood. The manufacturer seeking a factory site will find here detailed information as to the materials conveniently obtainable in the Humber area, and the industrial chemist with no such aim will also find the booklet very informative. Ten pages are occupied by a list of materials imported into Hull, and their uses. Industries already established in the neighbourhood furnish a variety of products required in modern chemical manufacture, notably alcohol and a host of organic solvents, the nature and applications of which are set out in Tables and Charts. A condensed, but very lucid, survey of some recent developments in the manufacture of synthetic products, including artificial resins, plastics, emulsifying agents, silicon products, and so forth, occupies nearly half the book. There are no statistics nor quantitative data; the book is well indexed, and in a small compass places a surprising number of modern products in their industrial setting.

J. H. Lane

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society with the Food Group of the Society of Chemical Industry was held on Wednesday, February 3rd, 1937, at the Chemical Society's Rooms, Burlington House. It was held in two sessions, at the first of which the chair was taken by Dr. G. Roche Lynch, President of the Society, and at the second by Dr. L. H. Lampitt, in the absence of the Chairman of the Food Group.

Certificates were read in favour of:—William Mitchell Cameron, James Laurence Campbell, B.Sc., Frank James Griffin, B.Sc., Herbert Clewin Griffith, Robert Edmund Richard Grimmett, M.Sc., F.N.Z.I.C., Eric Kennedy, B.Sc., A.I.C., Robert Hay McKinlay, F.I.C., John Aitken Macnair, F.I.C., Geoffrey William Martin, Enid Marian Pope, B.A., B.Sc., Archibald Rayner, B.Sc., F.I.C., William James South, Edward Taylor-Austin, A.I.C., John Ezra Woodhead, B.Sc., F.I.C., Ph.C., James Hunter Young, B.Sc., A.I.C.

The following were elected members of the Society:—Granville Hubert Clarke, Leonard Cartlidge Dutton, A.I.C., John Charles Giblin, B.Sc., A.I.C., Ronald William Gillham, Ph.C., Ronald Murray Hamilton, Walter Thomas Lunt, B.Sc., A.I.C., William Douglas McFarlane, M.A., Ph.D., William Stewart Patterson, Ph.D., M.Sc., F.I.C., Thomas Charles Williams, B.Sc., A.I.C., George Henry Wray.

The Meeting was devoted to a discussion on

THE LESS-KNOWN CONSTITUENTS OF MILK AND THEIR EXAMINATION.

The following papers were read and discussed:—"Some Minor Component Acids in Milk-fat and their Possible Significance," by Professor T. P. Hilditch, D.Sc., F.I.C.; "The Oxidation-Reduction Systems in Milk," by R. T. S. Twigg, B.Sc.; "Some Recent Work on the Lipase and Phosphatase of Cow's Milk," by Professor H. D. Kay, O.B.E., Ph.D., D.Sc., E. C. V. Mattick, M.Sc., Ph.D., and S. J. Folley, M.Sc., Ph.D.; "Present Knowledge of the Minor Nitrogenous Constituents of Milk," by J. H. Bushill, D.Sc., A.I.C., L. H. Lampitt, D.Sc., F.I.C., and D. F. Filmer, B.Sc.; and "The Estimation of Catalase in Milk," by E. B. Anderson, M.Sc., F.I.C., and R. MacWalter, Ph.D.

NORTH OF ENGLAND SECTION

THE Twelfth General Annual Meeting of the Section was held in Manchester on February 6th, 1937. The Chairman (A. R. Tankard) presided over an attendance of twenty-eight.

The Secretary presented the report and financial statement, which were adopted.

The following appointments for the coming year were made:—*Chairman*, A. R. Tankard; *Vice-Chairman*, Prof. T. P. Hilditch; *Committee*, W. F. Elvidge, J. Evans, S. E. Melling, Miss M. Roberts, C. A. Scarlett, J. R. Walmsley; *Honorary Auditors*, U. A. Coates, J. W. H. Johnson; *Honorary Secretary and Treasurer*, J. R. Stubbs.

The Chairman delivered the Annual Address, entitled "Chemical and General Scientific Control for Local Authorities."

The following paper was read and discussed:—"Notes on the Addendum, 1936, to the British Pharmacopoeia, 1932," by J. R. Walmsley, F.I.C.

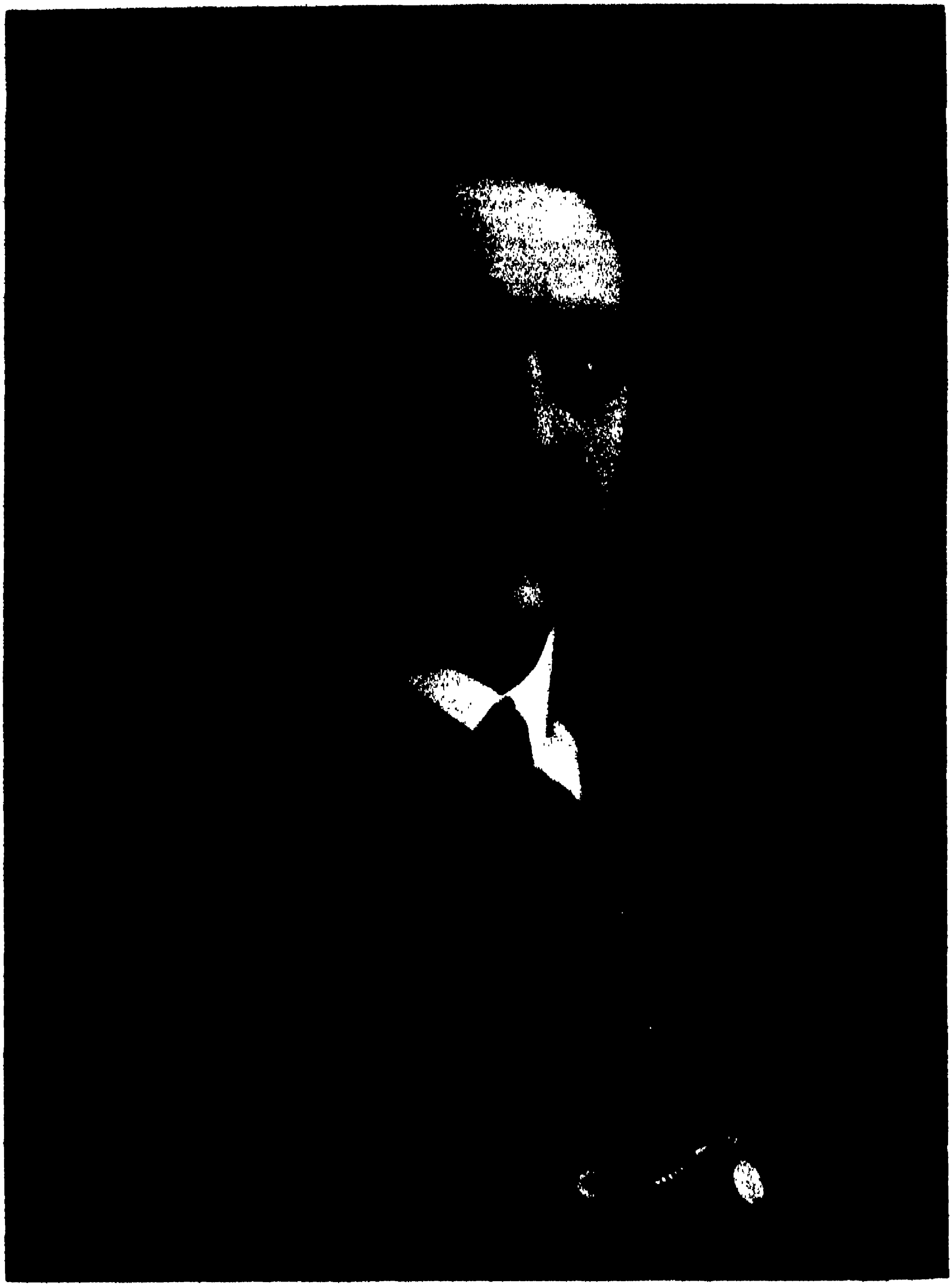
Obituary

PERCY ANDREW ELLIS RICHARDS, F.I.C.

ON the 22nd of December, 1936, there passed from our midst one who gave of his best to our Society and who in his time bore its highest honour, one who came only just a little too late to be considered among its actual founders, but whose work on its behalf is unsurpassed for enduring and consistent loyalty. For seventeen years he was one of our Honorary Secretaries, having as partners in this post the late A. Chaston Chapman and then E. Richards Bolton. At the end of this period his services were recognised by promotion to the Presidential chair. Afterwards, as Past President, he still held dear the interests of the Society and worked for it as long as strength was given him.

Born in 1868, he was educated at St. Paul's School and King's College, London, and studied analytical chemistry under the late Professor C. W. Heaton, having as fellow students Edward Russell and the late S. A. Vasey. With Vasey he was afterwards associated in joint work for *The Lancet* Laboratory. Heaton held the appointment of Lecturer in Chemistry and Physics at Charing Cross Hospital, and was succeeded in it by Richards. On the passing of his chief Richards set up in practice as consulting and analytical chemist, and was soon appointed Public Analyst for the parish of St. Martin-in-the-Fields. When various parishes were united to form the City of Westminster he remained as one of the three Public Analysts for the City, jointly with Col. C. E. Cassal and Mr. C. H. Cribb. A few years later he was appointed Public Analyst for the borough of Hammersmith. For many years he acted as Honorary Analyst to Charing Cross Hospital, and his interest in medical chemistry and toxicology led to his being consulted in some famous cases.

During his many years in practice he was responsible for work upon preservatives in imported meat, on the "facing" of rice, and on vinegar, for the Local



D. W. Richards

Government Board—now the Ministry of Health—the results of which are embodied in official communications. He also served as the Society's representative on the Departmental Committee on Preservatives and Colouring Matters in Food, appointed by the Minister of Health in 1923, and in 1925 as a member of the Departmental Committee on Improvers in Flour. In 1906 he served on the Advisory Committee on Drugs and acted as Honorary Secretary to this Committee.

Richards was a Fellow of the Chemical Society, and was also a loyal and active Fellow of the Institute of Chemistry, on the Council of which he served for two periods—1901 to 1904, and 1914 to 1917; from 1906 to 1909 he acted as Honorary Auditor to the Institute, and in 1910 was appointed Examiner in Branch E, which post he held for the usual four years.

To dwell upon his services to our Society, or to recount the many papers that he contributed to THE ANALYST, is not necessary here, for they are well known to us. His communications to *The Lancet* and other journals are, perhaps, less familiar because they deal with subjects somewhat removed from the usual work of Public Analysts. He wrote upon the saline waters of Boston Spa and of Salsomaggiore, as well as upon the determination of platinum in alloys and on the determination of iron in animal organs. It is interesting to recall that he was associated with Dr. William Hunter in researches on pernicious anaemia, especially with regard to the accumulation of iron in the liver, kidneys and spleen in this disease; he carried out large numbers of determinations of iron in these organs.

Analytical chemistry, though the chief part of his work, was yet only a part. As a teacher he held the post at Charing Cross Hospital already mentioned, and subsequently that of Lecturer in Chemistry and Metallurgy at the Royal Dental Hospital, combining these with his appointment as Professor of Chemistry at Queen's College, London. His merits as a teacher are recalled with gratitude by the writer and all the old students of Charing Cross and the Royal Dental Hospitals and of Queen's College; his kindly and painstaking manner endeared him to us all, no less than his powers of lucid exposition of the more difficult subjects evoked our admiration. In his early days he wrote a small textbook on practical chemistry for medical students, which, when subsequently enlarged to cover a wider syllabus, became probably the best-known work on the subject in medical schools.

It might be thought that these two spheres of activity were enough to fill one life, but in addition to serving on various councils and committees at the institutions wherein he taught, he found time to apply, very successfully, his financial ability to the service of Queen's College as Bursar and the Royal Dental Hospital as Honorary Treasurer. These duties, so many and so varied, he performed very conscientiously and with distinction; if only he had spared himself a little, he might, perhaps, never have suffered that breakdown in health which robbed us of his presence.

His last years were full of a wistful longing to get back to the things of the practical scientific world. Those of us who could sense this tried to make him feel that, although he was no longer active within our circle, he was still a valued member of it and very much in our thoughts. But the busy world left us little time to do more than outline to him the ever new happenings within it, though the eagerness with which he followed the tale and enquired about his friends showed all too plainly that he still had their welfare and that of our profession very much at heart. During these years what weighed most heavily upon him was his enforced idleness at a period when many notable advances were being made in the branch of knowledge which he had made his own. In these advances he was well equipped to take a leading part, and it is sad to ponder upon the loss of all that his co-operation might have brought us.

The unstinted and self-denying service which he rendered to chemistry has earned the lasting gratitude of chemists. F. W. EDWARDS

The Determination of Lead in Water

BY J. W. HAWLEY, B.SC., F.I.C., A.M.I.CHEM.E., AND W. WILSON, F.I.C.

(*Read at the Meeting of the Scottish Section, November* 19, 1936)

VARIOUS methods have been proposed from time to time for the analytical determination of lead in drinking water, the majority based on its colorimetric estimation as sulphide. Others include its precipitation as chromate,[1] followed by the determination of the latter by means of potassium iodide and thiosulphate, and the use of its peroxide,[2,3] formed chemically or by electrolysis, to produce the coloured hydroxy-tetramethyldiaminodiphenylmethane compound. The most recently introduced methods[4] employ organic reagents, notably dithizone—diphenylthiocarbazone.

[Technical Paper No. 4 of the Water Pollution Research Board (a publication of the greatest value to anyone interested in the problem) gives a summary of existing knowledge up to 1934. It would appear that in many cases the methods of analysis might give rise to serious error from the presence in the waters examined of other metals and substances.]

It is with amounts of lead of the order of 0·01 to 0·05 part per 100,000, generally in peaty water, that we have been mainly concerned, and the following note is a description of methods we have found satisfactory. These methods have now been in use for nearly two years.

For the detection of lead in water, the customary acetic acid and hydrogen sulphide test serves, provided that not less than 0·02 part of lead per 100,000 is present, that the sample is colourless or nearly so, and that it is compared with a control using a column of depth not less than 12 in. When the water is discoloured by vegetable matter, amounts of the order of 0·05 part of lead per 100,000 cannot always be detected with certainty. Such waters, particularly when the *p*H is below 7, may contain iron in amount sufficient to make the result uncertain, while the hydrogen sulphide exerts a bleaching action on the organic matter, so that the solution under test may actually appear lighter than the untreated control. In such cases, however, the dichromate test will generally demonstrate the presence of lead, although the opalescence may take some time to develop.

FIRST METHOD.—This consists simply of the relevant portions of the method devised by Francis, Harvey, and Buchan[5] for the determination of lead in urine.

The following solutions are required:—(1) Citric acid solution, 10 per cent.; (2) copper sulphate solution, 0·8 per cent.; (3) conc. sulphuric acid; (4) masked methyl orange indicator; 1 g. of methyl orange and 1·4 g. of xylene cyanol F.F. dissolved in 500 ml. of 50 per cent. alcohol; (5) ammonia, sp.gr. 0·880; (6) conc. nitric acid; (7) ammonium acetate solution, 10 per cent.; (8) potassium cyanide solution, 10 per cent.; (9) ammonia, 6 *N* (approx.); (10) sodium sulphide solution: sodium sulphide pure crystals 50 g., glycerin 50 g., water to 250 ml.; this solution is diluted with an equal bulk of water just before use. The reagents should all be of analytical reagent quality.

To 250 ml. of the sample contained in a conical flask are added 3 ml. of citric acid solution, 3 ml. of copper sulphate solution, 2 ml. of concentrated sulphuric acid and 2 to 3 drops of indicator. Concentrated ammonium hydroxide (sp.gr. 0·880) is now run in until the red colour gives place to purple and finally to a neutral grey. The addition of one or more drops produces a green tint, and the *p*H of the solution is then between 4 and 5. Hydrogen sulphide is now passed through the solution for an hour.

After standing for 15 to 30 minutes the liquid is filtered through an 11-cm. Swedish paper (No. 1. F), and the precipitate is washed twice with a saturated solution of hydrogen sulphide. The precipitate and paper are then transferred to a tall 250-ml. beaker. Nitric acid (1 to 2 ml.) is added to the original flask, which is then heated over a rose burner, and the acid with subsequent washings are added to the paper in the beaker. This recovers any precipitate still adhering to the walls of the flask. The paper containing the mixed sulphides is now destroyed by a wet combustion. Four or five ml. of nitric acid and 3 ml. of sulphuric acid are added to the contents of the beaker, which is then covered with a watch-glass and heated on the hot plate until a clear solution is obtained, further additions of nitric acid being made if necessary. When the oxidation is complete, the watch-glass is removed and the heating is continued until the excess of sulphuric acid has been expelled, the last traces being driven off by gentle blowing while the beaker is still hot.

The residue of mixed sulphates is treated with 10 ml. of water and conc. ammonia (sp.gr. 0·880) added dropwise until the colour of the solution is a deep blue; 25 ml. of water containing 1·5 ml. of nitric acid are then added, and the solution is ready for electrolysis.

The electrolysis is conducted with the electrodes and under the conditions prescribed by Francis, Harvey and Buchan, *i.e.* the electrodes are of platinum-iridium (25 per cent. of iridium). The anode is a cylinder 1 cm. deep and of 1 cm. diameter, and the cathode is 1½ cm. square; wires 12 cm. long are attached to both. The conditions are: temperature, 70 to 80° C.; voltage, 1·5 to 2; current density, 0·3–0·4 amp. per 100 sq.cm.; speed of rotation of anode 1500–2000 r.p.m.; period of electrolysis 1 hour.

We have found the following mechanical arrangement satisfactory:—The electrode wires pass through 2 small holes, 4 cm. apart, drilled in the watch glass which covers the tall 250-ml. beaker, that of the anode to the customary rotating holder, that of the cathode to a fixed holder.

Each rotating anode is driven directly from its own pulley fixed on a horizontal countershaft, which in turn is driven by a small series-wound motor. The speed of the motor is controlled by a variable resistance composed of a bank of lamps, and is measured by means of a revolution counter connected with the spindle of the motor by wheel and worm gearing.

A 4-volt accumulator connected with a distributing board supplies the current for electrolysis. On the board are mounted variable resistances and switches for controlling the currents passing to the electrodes, each pair of which has its own resistance and multiple switch. The last-named serves as an on/off switch and also permits of the insertion of a voltmeter and an ammeter in the circuit of any cell for test purposes without interrupting the electrolysis.

When the electrolysis is completed, the deposit of lead peroxide is dissolved by transferring the anode, after washing, to a Nessler glass containing about 10 ml. of water to which 2 to 3 drops of nitric acid and a crystal of potassium oxalate have been added.

From the appearance of the deposit an opinion can be formed of the approximate amount of lead present, and the entire solution or an aliquot portion can be used for the determination. The volume of the solution taken should be such that the amount of lead present is between 0·035 and 0·065 mg.

To the liquid under test are added 10 ml. of ammonium acetate solution, 2 ml. of potassium cyanide solution, 5 ml. of 6 *N* ammonia, and then water to 50 ml. The whole is mixed and allowed to stand for 2 to 3 minutes, after which 2 drops of sodium sulphide solution are added, the solution is again mixed, and the tint is compared immediately with standards.

The range of standards is prepared in a similar manner, varying volumes—0·5 to 1·5 ml. by increments of 0·2 ml.—of standard lead solution (1 ml. = 0·05 mg. of lead), with the appropriate addition of nitric acid and potassium oxalate, taking the place of the liquid under test.

It is essential that the sample and standards be prepared under as nearly identical conditions as possible, both as regards the order of addition of reagents and the nature and quantity of electrolyte present.

A control is carried out in exactly the same manner, but using distilled water instead of the sample, so that the necessary correction for lead present in the reagents, etc., can be made. This correction is small and should not exceed 0·2 ml. of standard lead solution.

Having regard to the exhaustive investigations made by the original authors numerous check experiments were considered superfluous. A few results are given below.

	Lead Parts per 100,000		
Water	Added	Found	Remarks
Distilled	Nil	Nil	"blank," 0·0012, 400 ml. used
Distilled	0·011	0·009	400 ml. used
Reservoir A	Nil	Nil	"blank," 0·0012, 400 ml. used
(Oxygen absorbed in 4 hours, 0·39 part)	Nil	Nil	"blank," 0·0018, 400 ml. used
	0·014	0·014	
	0·014	0·014	
	0·030	0·026	
	0·030	0·032	

This method has various advantages—gain of lead is unlikely, and there is little risk of loss, as the sulphide is precipitated directly with a large excess of copper. The wet combustion, though time-consuming, needs little or no attention. Electrolysis gives the lead free from interfering elements likely to be present, and in a form suitable for easy estimation. The separation of sulphate with alcohol is unnecessary, and the "blank" is low.

On the other hand, there are the troubles attendant on the filtration of relatively large volumes of a saturated solution of hydrogen sulphide—particularly noticeable in any building not used exclusively as a laboratory. The apparatus is expensive, especially the platinum portion, and although costly electrical instruments are not required, a low resistance ammeter is desirable. In addition, the operator must give considerable attention to the electrolysis.

SECOND METHOD.—This is the method we generally employ, as it is more suitable for batch working.

The solutions required are those previously described with the exception of No. 2 (copper sulphate). Potassium chlorate is also needed.

Two hundred and fifty ml. of the sample, acidified with 2 ml. of hydrochloric acid, are evaporated to about 5 ml. in a silica basin (or beaker) and allowed to cool. A few crystals of potassium chlorate and 1 ml. of conc. hydrochloric acid are then added, the basin is covered, and the contents are allowed to simmer for a short time over a rose burner. The cover is removed, and the sides of the basin are rinsed with the acid liquor and washed down with boiling water. A further 1 ml. of conc. hydrochloric acid is added, and the solution is boiled until free from chlorine. The hot solution is then filtered through a 5·5-cm. No. 41 Whatman paper into a 50-ml. conical flask, and the basin and paper are washed with boiling water. The total volume of the filtrate should not exceed 25 ml.

One ml. of citric acid solution and one drop of masked methyl orange are added to the cold filtrate, and ammonia (0·880) is next run in until the red colour of the indicator changes to purple, when the neutralisation is continued with 2 *N* ammonia until the purple colour changes to a grey tint and finally to green. Care must be taken that the final change to green is effected with a single drop of ammonia. If the end-point is overstepped, hydrochloric acid must be added to restore the purple colour, and then 2 *N* ammonia until the proper end-point is reached. Hydrogen sulphide is next passed through the solution for 45 minutes.

The precipitate is allowed to settle, the solution is filtered through a 5·5-cm. Swedish paper (No. 1. F), and the flask and precipitate are washed twice with a saturated solution of hydrogen sulphide. The lead sulphide on the paper is dissolved in 1 ml. of conc. nitric acid, the filtrate being received in a 100-ml. beaker. To ensure the complete removal of the precipitate from the flask, a few drops of nitric acid are added, and the contents are heated gently over a rose burner, the acid and subsequent washings being passed through the filter. When washing is completed 10 drops of conc. sulphuric acid are added to the contents of the beaker, which are then evaporated to dryness on the hot plate, and allowed to cool. Five ml. of ammonium acetate solution are added, the beaker is covered, and the contents, after boiling for a few minutes, are filtered through a 5·5-cm. No. 41 Whatman paper into a 50-ml. Nessler glass. A further 5 ml. of ammonium acetate solution are added to the beaker, and the liquid is boiled and filtered through the same paper, which is then washed with boiling water containing a little ammonium acetate until the volume of the filtrate is about 30 ml.

Whether the entire volume of the filtrate or only an aliquot part should be used for estimation can generally be decided from the appearance of the sulphide precipitate. As stated earlier, the volume of solution taken should be such that the amount of lead present lies within the limits 0·035 and 0·065 mg. When an aliquot portion is taken, sufficient ammonium acetate solution should be added to bring the total amount in the Nessler cylinder up to 10 ml. To the liquid under test are added 2 ml. of potassium cyanide solution, 5 ml. of 6 *N* ammonia, and water to 50 ml. The whole is mixed and allowed to stand for 2 to 3 minutes. Two drops of sodium sulphide solution are next added, the solution is again mixed, and the tint is compared immediately with standards.

To prepare the range of standards, varying volumes of 0·5 to 1·5 ml. by increments of 0·2 ml. of standard lead solution (1 ml. = 0·05 mg. of lead) are added to Nessler cylinders, each containing 10 ml. of ammonium acetate solution. Additions of potassium cyanide and ammonia, etc., are made in the manner just described, the sample and standards being prepared under as nearly identical conditions as possible.

A control, using distilled water to replace the sample, enables the necessary correction to be made for lead present in the reagents and gained from the apparatus, etc.

The correction (blank) in this method is greater than in the first method, but should not exceed 0·4 ml. of standard lead solution.

In a series of tests the following results were obtained:

	Lead Parts per 100,000		
Water	Added	Found	Remarks
Distilled	0·008	0·010	"blank," 0·008
	0·011	0·009	"blank," 0·007
	0·020	0·021	
	0·028	0·026	
	0·038	0·038	
Reservoir A (oxygen absorbed in 4 hours 0·39 part)	0·014	0·017	"blank," 0·008
	0·014	0·016	"blank," 0·007
	0·030	0·031	
	0·030	0·025	
Composite (oxygen absorbed in 4 hours 1·0 part)	0·010	0·009	"blank," 0·005
	0·014	0·019	
	0·020	0·023	
	0·039	0·035	
	0·048	0·051	
Water containing lead (oxygen absorbed in 4 hours 0·44 part)	Nil	0·012	"blank," 0·008
	0·006 (0·018)	0·016	500 ml. used
	0·012 (0·024)	0·024	
	0·018 (0·030)	0·030	
	0·024 (0·036)	0·040	
	0·030 (0·042)	0·044	

In this method it is only necessary to filter small volumes of hydrogen sulphide water, and, as the precipitated lead sulphide is dissolved from the paper, the wet combustion is merely that of the small amounts of paper fibre which have become detached by the acid and wash liquors. In the presence of much zinc or iron the electrolytic method is necessary.

THIRD METHOD.—This consists of a combination of the two preceding methods and is useful when lead and copper are present together. The procedure adopted follows that of the second method as far as the precipitation and filtration of the sulphides. The paper and precipitate are then transferred to a 250-ml. tall beaker, and a wet oxidation is carried out as in the first method. The resulting solution is electrolysed without previously coating the cathode with copper. So far we have not examined the influence (if any) of the absence of a preliminary copper deposit on the cathode, but the separation appears to be satisfactory. When electrolysis is completed the anode is removed and any solution adhering to it is washed back into the beaker. The deposit of lead peroxide is then dissolved, and the lead is determined in the usual way.

The copper which has separated on the cathode during electrolysis dissolves in the electrolyte on breaking the circuit. The electrode is removed and washed. Two ml. of hydrochloric acid are added to the beaker, and the contents are evaporated to dryness on the hot plate. The residue is taken up with dilute hydrochloric acid and the copper is estimated colorimetrically as ferrocyanide.

As described, these methods give satisfactory results when the amount of lead present is 0·01 part (or more) per 100,000. With smaller amounts not less than 500 ml. of the sample should be taken.

SUMMARY.—Two methods are described for the separation and determination of lead in drinking water.

(1) *Electrolytic Method.*—(*a*) The lead is precipitated directly as the sulphide in the presence of a large excess of copper, the solution being previously buffered to a *p*H value between 4 and 5.
  (*b*) The mixed sulphides are filtered off and washed with saturated hydrogen sulphide water.
  (*c*) The paper containing the sulphides is destroyed by a wet combustion.
  (*d*) The lead is separated from this solution as peroxide by electrolysis.
  (*e*) The deposited lead peroxide is dissolved from the electrode and the lead estimated colorimetrically as the sulphide.

This method is recommended when the highest degree of precision is desired and when the water is further contaminated by other metals.

(2) *Concentration Method.*—(*a*) The water is acidified and concentrated to a small volume.
  (*b*) The organic matter in the concentrated water is oxidised by potassium chlorate in the presence of hydrochloric acid.
  (*c*) The solution is buffered to a *p*H value 4 to 5, and the lead is precipitated as sulphide.
  (*d*) The sulphide is collected on a filter-paper, washed, and dissolved in conc. nitric acid.

(*e*) The solution is evaporated to dryness with sulphuric acid to destroy any filter-paper fibres present.

(*f*) The lead sulphate is dissolved by boiling with a solution of ammonium acetate, and, after filtration, the lead is estimated colorimetrically as sulphide.

This method is recommended where a large number of samples have to be examined, since determinations can be made conveniently in batches of from six to eight. By connecting the flasks in series, one Kipp apparatus suffices for "gassing."

This method should not be used in the presence of zinc or of much copper or iron.

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COUNTY LABORATORY
DUMFRIES

The Determination of Benzoic Acid

BY F. W. EDWARDS, F.I.C., H. R. NANJI, PH.D., D.I.C., F.I.C., AND
M. K. HASSAN, M.SC.

(*Read at the Meeting, November* 4, 1936)

PART I. MODIFICATION OF NICHOLLS'S METHOD

THE partial conversion of benzoic acid into salicylic acid by hydrogen peroxide was first noticed by Hanriot,[1] but no attempt was made to apply the test—which is often described as Jonescu's test—to the determination of this acid until Nicholls[2] studied exhaustively the optimum conditions, particularly those under which the proportion of salicylic acid produced was constant. Nicholls found that:—(1) Small quantities of benzoic acid were readily oxidised to salicylic acid by hydrogen peroxide in slightly acid solution in the presence of iron salts, and that rise of temperature enhanced the rate of oxidation. (2) Under standardised conditions of concentration of mineral acid, hydrogen peroxide and ferric chloride, the proportion of benzoic acid converted was about 12 per cent., and this proportion was fairly constant up to a maximum concentration of benzoic acid (5 mg. in 15 ml.).

The amount of salicylic acid formed was determined either by the ferric salicylate test or by Jorissen's test. In applying the ferric salicylate test after oxidation it is essential to regulate the acidity within a narrow limit—about 0·002 *N*—since the depth of colour and the tint vary appreciably with the acidity of the solution. Nicholls added a fixed amount of alkali after oxidation and filtered the solution, this procedure being adopted to remove the bulk of the iron salt, which would otherwise interfere in the colorimetric stage, as well as to regulate the acidity of the filtrate. Whilst we obtained fairly satisfactory results when working on pure benzoic acid, we were not always successful in getting the proper violet tint in dealing with extracts of the acid from food products, probably because of the difficulty of adjusting the acidity of the final solution.

We therefore attempted to modify the method so as to avoid the necessity of regulating the acidity. The procedure which we found very successful was to extract the salicylic acid from the cooled oxidation mixture by means of ether and, after removal of the solvent, to dissolve the residue in 10 per cent. alcohol and determine the salicylic acid colorimetrically as ferric salicylate. The *p*-hydroxybenzoic acid and possibly dihydroxy-benzoic acids, which are simultaneously formed, do not interfere if the iron solution used in the colorimetric stage of the process is distinctly acid (see p. 179). The procedure also eliminates the necessity for a blank test, the colour match obtained by using a salicylic acid standard in 10 per cent. alcohol being quite satisfactory.

We have also made a few other comparatively minor modifications in order further to standardise the method, and these may be noted here:—(i) The oxidation is carried out in a distinctly acid solution by the addition of 5 ml. of 0·1 *N* sulphuric acid prior to oxidation; this prevents the possibility of precipitation of the iron salt before the oxidation is complete. (ii) The solution is heated by immersion in a boiling water-bath for 15 minutes, this being found the optimum time (see Table I). (iii) The strength of hydrogen peroxide is doubled, as this gives a definite increase in the yield of salicylic acid under our conditions.

In Table I are recorded the results of experiments wherein 5 mg. of benzoic acid were oxidised after addition of 5 ml. of 0·1 *N* sulphuric acid, time of heating and concentration of hydrogen peroxide being varied. The optimum concentration of hydrogen peroxide is therein shown to be 1 ml. of 0·2 per cent. in the 15 ml. of reaction mixture, and 15 minutes' heating is shown to be the period for the maximum yield of salicylic acid.

TABLE I

		Salicylic acid found		
Benzoic acid taken mg.	Time of heating Minutes	1 ml. 0·1 per cent. hydrogen peroxide mg.	1 ml. 0·2 per cent. hydrogen peroxide mg.	1 ml. 0·4 per cent. hydrogen peroxide mg.
5	3	—	0·39	—
5	5	0·29	0·41	0·41
5	9	0·32	0·44	0·44
5	12	0·33	0·45	—
5	15	0·35	0·46	0·41
5	18	—	0·46	—

The modified method found satisfactory for foods and drugs is as follows:

REAGENTS REQUIRED.—(i) *Iron reagent A for oxidation*: a solution of 2·7 g. of anhydrous ferric chloride in 13 ml. of *N* sulphuric acid made up to 100 ml. with water; (ii) 0·2 *per cent. hydrogen peroxide solution* prepared by diluting 2 ml. of "20 vol." solution to 60 ml. with water; (iii) *standard sulphuric acid*, 0·1 *N*; (iv) *standard salicylic acid*: a solution in 10 per cent. alcohol, 1 ml. containing 0·1 mg.; (v) *iron reagent B for colorimetric determination*: a solution of 0·1 g. of anhydrous ferric chloride in 20 ml. of *N* hydrochloric acid diluted to 100 ml. with water; this solution gives a very clear violet tint with salicylic acid and eliminates the possible interference of *p*-hydroxybenzoic acid and other compounds.

EXPERIMENTAL DETAILS.—The benzoic acid is isolated from the sample either by direct extraction with an immiscible solvent or by steam distillation from an acid solution saturated with salt (*cf.* Monier-Williams[3]).* In either case the acid is converted into its ammonium salt by adding dilute ammonia, and the excess of ammonia is removed by boiling in a conical flask until no odour of ammonia is noticed and the vapours are neutral to litmus paper. The solution of ammonium benzoate is then made up to a definite volume.

An aliquot portion of this solution, containing not more than 5 mg. of benzoic acid, is taken for oxidation in a boiling-tube (6 × 1 in.), 5 ml. of 0·1 *N* sulphuric acid is added, and the volume is adjusted to 15 ml. with distilled water; 1 ml. of iron reagent A and 1 ml. of hydrogen peroxide are then added, and the whole is well mixed and heated in a boiling water-bath for 15 minutes *without further shaking.* The solution, which becomes deep violet in colour, is well cooled, about 5 g. of ammonium sulphate are added, and the salicylic acid is extracted with three successive quantities of 15 ml. of ether, each ethereal extract being washed with 5 ml. of water.

The solvent is then completely removed by distillation on a water-bath at 50° C., the residue is dissolved in 50 ml. of 10 per cent. alcohol, 1 ml. of iron solution B is added, and the violet colour produced is compared with the salicylic acid standard made up to 50 ml. with 10 per cent. alcohol.

Under the conditions described 1 mg. of benzoic acid gave approximately 0·1 mg. of salicylic acid, although it should be pointed out that under all the conditions that we have tried a definite gradation was always observed in the proportion of benzoic acid oxidised, according to the amount originally present. This is clearly shown in Table II. It is therefore not strictly permissible to use a fixed ratio in the determination of benzoic acid from the salicylic acid formed. From the results obtained Table III has been constructed, in which the amounts of salicylic acid formed are correlated with the quantities of benzoic acid originally present. This Table, which is an inverse form of Table II, with interpolations, affords a more ready means of converting the quantity of salicylic acid found into terms of benzoic acid.

TABLE II

Benzoic acid taken, mg.	5	4	3	2	1
Salicylic acid found, mg.	0·45	0·41	0·32	0·22	0·13
	0·46	0·42	0·33	0·22	0·13
Benzoic acid converted, per cent.	9·1	10·35	10·55	11·0	13·0

TABLE III

Salicylic acid formed on oxidation, mg.	0·1	0·15	0·2	0·25	0·3	0·35	0·4	0·45
Benzoic acid originally present, mg.	0·77	1·25	1·8	2·3	2·8	3·3	3·85	5·0

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* The possibility of the formation of maltol by sugary material in this process must be borne in mind. In this and some other cases a preliminary oxidation with alkaline permanganate, as described later, may be necessary.

The following are a few typical results obtained with some ordinary cordials to which known amounts of benzoic acid were added:

TABLE IV

Sample and quantity taken	Benzoic acid added mg.	Benzoic acid found mg.
Peppermint cordial (50 ml.) ..	17	16·5
Raisin wine (50 ml.)	15	14·2
Orange squash (25 ml.) ..	5	4·9

The method herein described is, in our experience, one of the most sensitive for the *detection* of benzoic acid in food, as 0·5 to 1·0 mg. can be found easily. Moreover, the test is specific; so far as is known, it is given by no other substance, except saccharin,* likely to be present in food.

We have also found the method a rapid and useful one for the *determination* of benzoic acid in food. In a few instances we have compared the results with those obtained by Mohler's test as modified by Illing.[4] This is also a very good test, but unfortunately it is by no means specific for benzoic acid. Also, the accuracy of the method of determination based upon the test depends to a large extent on the stated time being allowed for nitration and strict adherence to other details. The results obtained when the method was strictly followed agreed well with those obtained by Nicholls's method.

PART II. DETERMINATION OF BENZOATES AND SALICYLATES IN PRESENCE OF ONE ANOTHER

The determination of benzoic acid and of salicylic acid in presence of one another is sometimes required, especially in some antiseptic medicines—such as Glycerinum Thymolis Co., B.P.C.—and not infrequently in foreign canned goods.

DETERMINATION OF SALICYLIC ACID.—Of the methods for the determination of salicylic acid in presence of benzoic acid, that of Autenrieth and Beuttel,[5] which consists in precipitating and weighing salicylic acid as tribromophenol bromide, gives good results, but it is somewhat lengthy. The volumetric modification of it (*cf.* B.P. *Assay of Phenol*) is both rapid and accurate for pure salicylic acid, but its use is limited when working on extracts of salicylic acid from food or drugs. We have found that the ferric salicylate test and the Jorissen test, as described below, are satisfactory for determining salicylic acid in presence of benzoic acid.

THE FERRIC SALICYLATE TEST.—In applying this test, if the iron solution B, which is distinctly acid, is used in the colorimetric determination, it will be found sensitive to as little as 0·1 mg. of salicylic acid in 50 ml. in presence of 15 mg. of benzoic acid. In the experiments recorded in Table V, varying amounts of benzoic acid (added as aqueous solution of sodium benzoate), and salicylic acid (added as a solution of the free acid in dilute alcohol) were mixed with 50 ml. of water, 1 ml. of the iron solution B was run in, and the violet colour produced was compared with the salicylic acid standard.

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* This substance, if present, should be separated from benzoic acid by extraction of the latter with carbon tetrachloride, in which saccharin is almost insoluble.

TABLE V

Benzoic acid added mg.	Salicylic acid added mg.	Salicylic acid found by ferric salicylate test mg.	Salicylic acid found by Jorissen's test mg.
3	0·1	0·11	0·10
5	0·1	0·10	0·10
10	0·1	0·11	0·10
15	0·1	0·10	0·10
10	0·3	0·29	0·30
15	0·3	0·30	0·31
10	0·4	0·41	0·40
15	0·4	0·41	0·40
10	Nil	No colour	No colour
15	Nil	,, ,,	,, ,,

THE JORISSEN TEST.—Nicholls worked out the best conditions for carrying out this test; these are briefly noted below. It has given excellent results in our hands, and is the most suitable of those available for confirming the presence of salicylic acid and also for its determination in the presence of benzoic acid.

Reagents.—(i) A 2 per cent. solution of sodium nitrite; (ii) a solution containing 0·3 per cent. of crystallised copper sulphate in 10 per cent. acetic acid; (iii) standard colour solution prepared by carrying out the test as described below on 5 ml. of 0·1 per cent. salicylic acid solution diluted to 40 ml., using 5 ml. of each of the reagents (i) and (ii), and diluting the final solution to 100 ml., 1 ml. of this standard colour being therefore equivalent to 0·05 mg. of salicylic acid.

The Test.—To the mixture of benzoic and salicylic acids in about 25 ml. of water are added 1 ml. of each of the reagents (i) and (ii), and the mixture is heated in a boiling water-bath for 15 minutes, cooled, and diluted to 50 ml. The red colour produced is matched by adding the standard colour solution from a burette to a blank consisting of 50 ml. of water containing 1 ml. of reagent (ii).

The degree of accuracy which was attained by this method in our experiments is clearly indicated in Table V.

DETERMINATION OF BENZOIC ACID.—Although it is easy to ***distinguish*** benzoic from salicylic acid by Mohler's test as modified by Illing (*loc. cit.*),[4] this test cannot be used for the ***determination*** of benzoic acid when salicylic acid is also present, because the latter also responds, giving a yellow to brownish-yellow colour. We found that Nicholls's method, as modified in the present communication, gives good results if the salicylic acid is first destroyed by alkaline permanganate (*cf.* von der Heide and Jacob).[6]

Preliminary experiments were made upon a solution containing 10 mg. of salicylic acid (as the sodium salt) and 15 mg. of benzoic acid. The salicylic acid was then selectively oxidised by adding 5 ml. of 0·1 *N* potassium hydroxide solution, warming to about 50° C. and adding *N* potassium permanganate solution until a persistent pink colour was observed, about 5 ml. being required. The mixture was acidified with 5 ml. of dilute sulphuric acid (1 in 3), and 10 per cent. oxalic acid solution was added, drop by drop, until a colourless solution was obtained. The benzoic acid was extracted with ether after saturating the solution with ammonium sulphate, the ethereal extract was washed with water, and the acid was converted into its ammonium salt by two or three shakings with dilute ammonia. The excess ammonia was boiled off, the solution was diluted to 30 ml., and 10 ml. of this (representing 5 mg. of benzoic acid) were taken for the determination as described on p. 175.

The amount of salicylic acid found varied from 0·43 mg. to 0·47 mg. Taking the average, reference to Table III will show that the equivalent of benzoic acid indicated is 5 mg.

The application of these methods to the simultaneous determination of benzoates and salicylates in compound glycerin of thymol, B.P.C., may be quoted as an illustration of their use in a particular case:

Twenty ml. of the sample were diluted to 100 ml., and 20 ml. of this solution were shaken with small quantities of ether to remove the bulk of the volatile oils, etc., and then acidified with dilute sulphuric acid, and the benzoic and salicylic acids were extracted by repeated shakings with ether after partial saturation with ammonium sulphate. The mixed ethereal extracts were washed two or three times with 10-ml. portions of water to remove the colouring matter, the usual precautions to avoid loss of the acids being taken. The acids were then converted into their ammonium salts, and after excess of ammonia had been boiled off, the solution was cooled and diluted to 100 ml. (Solution A).

The salicylic acid was determined in 1 to 2 ml. of this solution by the Jorissen test or colorimetrically as ferric salicylate.

The amount of sodium salicylate found in different samples varied from 0·45 per cent. to 0·52 per cent., the B.P.C. formula requiring 0·52 per cent.

For the determination of benzoic acid 20 ml. of Solution A were taken, the salicylic acid was destroyed by oxidation with alkaline permanganate, and the subsequent oxidation of the residual benzoic acid to salicylic acid and the determination of the latter were carried out as described on p. 176.

The amount of sodium benzoate found in different samples varied from 0·65 per cent. to 0·82 per cent., the B.P.C. formula requiring 0·8 per cent.

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ROYAL DENTAL HOSPITAL
LEICESTER SQUARE, W.C.2

The Detection and Determination of *p*-Hydroxybenzoic Acid and its Derivatives, with special reference to their Distinction from Salicylic and Benzoic Acids

By F. W. EDWARDS, F.I.C., H. R. NANJI, PH.D., D.I.C., F.I.C., AND
M. K. HASSAN, M.Sc.

(*Read at the Meeting, November* 4, 1936)

THE use of *p*-hydroxybenzoic acid,* its sodium salt and its esters, as food preservatives is now quite well known. Of the esters, the commonest are Nipagin A, the ethyl ester; Nipagin M, also known as Solbrol, which is the methyl ester; and Nipasol M, the propyl ester.

Sabalitschka[1] found the propyl ester to be the most effective generally, although the methyl ester was more specifically antiseptic in some cases.

In some foreign countries the use of para-acid and its esters as preservative, either singly or as a mixture, is permitted (*cf.* ANALYST, 1934, 59, 348); they are also used as preservatives for pharmaceutical preparations. In this country the Preservatives Regulations prohibit the use of these compounds, and imported canned goods have frequently to be examined for them. Recently we had reason to suspect the presence of para-acid in imported tins of smoked salmon,[2] and we could find few methods for detecting this acid and its derivatives or for distinguishing them from those of its ortho-isomer, salicylic acid. Although some work had been published (*cf.* Weiss,[3] and Blicke and Smith[4]) the information available on the subject was scanty, and we had to develop methods of detecting para-acid and its esters and of distinguishing them from salicylic and benzoic acids.

ISOLATION OF SALICYLIC, BENZOIC AND *p*-HYDROXYBENZOIC ACIDS.—Since para-acid may be used in admixture with its esters, the general procedure adopted was to extract these mixed preservatives by means of an organic solvent, such as alcohol or ether, to hydrolyse them with alcoholic potash, and to isolate the acids as their ammonium salts in neutral solution.

The following seven tests were applied to the solutions thus obtained.

I. TEST WITH MILLON'S REAGENT.†—If 20 ml. of the neutral solution of the ammonium salt of para-acid, salicylic acid or benzoic acid, containing the equivalent of as little as 0·1 mg. of the respective acids, is treated with 2 ml. of Millon's reagent and the mixture is heated in a boiling water-bath for two minutes, a red colour is obtained with both salicylic acid and para-acid, whilst benzoic acid gives no colour.

The colours obtained with the two former acids, when compared side by side,

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* This acid will usually be referred to as "para-acid" in this communication.

† Millon's reagent gives the best results when prepared as follows:—One part by weight of mercury is dissolved in twice its weight of conc. nitric acid, with gentle warming. The solution obtained is diluted with twice its volume of water. The *freshly prepared* reagent is more sensitive than one that has been kept, and gives a much deeper shade of red.

COPPER *p*-HYDROXYBENZOATE (× 25).

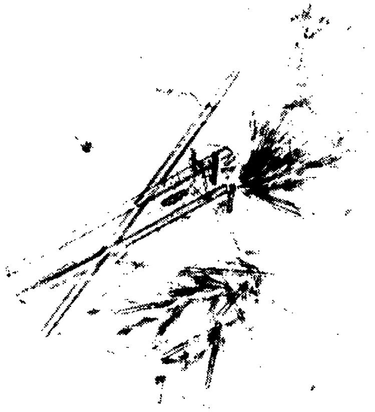

Fig. 1. Slow crystallisation.

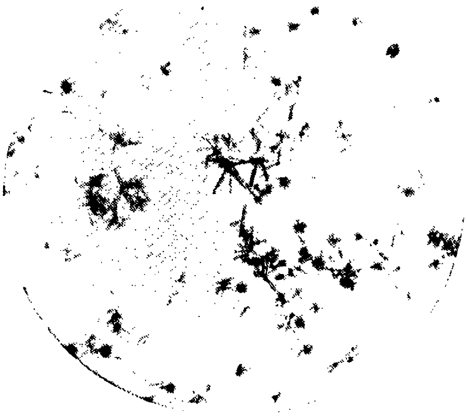

Fig. 2. Rapid crystallisation.

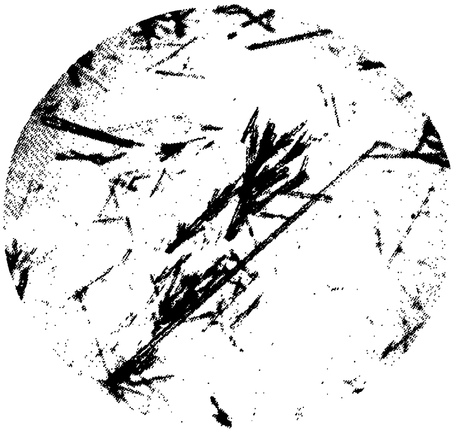

Fig. 3. Slow crystallisation.

are quite distinct, that with para-acid being rose-red and that with salicylic acid being orange-red, but one cannot always rely upon these differences in tint, although they give valuable indications.

This reaction is given by nearly all aromatic substances containing a hydroxyl group attached to the benzene nucleus, and is one of the most sensitive tests for para-acid and salicylic acid in foods; the non-appearance of a red colour within five minutes is a certain proof of the absence of these two acids. If a positive reaction is obtained, confirmatory tests are advisable.

II. FERRIC CHLORIDE TEST.—The contradictory statements published as to the action of ferric chloride solution on para-acid are probably due to the use of different quantities of the acid and different acidities of ferric chloride solution. We obtained the following reactions on adding 1 ml. of the iron reagent B (p. 174) to different quantities of para-acid dissolved in 50 ml. of water:—Five mg., no colour; 10 mg., very slight violet colour; 15 mg., faint violet colour equivalent to that obtained with 0·1 mg. of salicylic acid.

It would therefore appear that salicylic acid is approximately 150 times as sensitive as para-acid in this test when carried out in the manner indicated. Benzoic acid, of course, gives no colour. The possibility that the violet colour is due to traces of salicylic acid present as an impurity in the para-acid has yet to be investigated.

If the Millon test is positive and the ferric chloride test is negative, the absence of salicylic acid is proved, whilst the presence of para-acid is strongly indicated. If, however, the ferric chloride test is also positive, either salicylic acid alone or both acids may be present.

III. JORISSEN'S TEST.—About 10 to 25 ml. of the solution of ammonium salt should be tested exactly as described on p. 176. As little as 0·1 mg. of salicylic acid gives a distinct pink colour. With para-acid under the same conditions 1 mg. gives a very faint yellow colour, and even when the quantity is increased to 10 mg. in 25 ml. of the solution the colour produced is distinctly yellow, not pink. Benzoic acid gives no colour in Jorissen's test. As already stated (p. 176), the test is the most suitable for confirming the presence of salicylic acid. Therefore, a positive Millon test with a negative Jorissen test proves the absence of salicylic acid and raises a strong presumption of the presence of para-acid. Obviously, if the Jorissen test is also positive the presence of salicylic acid is proved, but not necessarily the absence of para-acid.

IV. COPPER-SALT CRYSTALS.—This test depends on the fact that the copper-salt of para-acid is relatively insoluble in water and crystallises out, whereas copper salicylate is very soluble. The appearance of the crystals under the microscope is very distinctive, as will be seen in the photomicrographs (see Plate: Figs. 1, 2 and 3).

The best conditions for this test were achieved by evaporating an aliquot part of the neutral solution of the ammonium salt containing not less than the equivalent of 2 mg. of para-acid (preferably 5 mg.) with 1 ml. of 2 per cent. aqueous copper sulphate solution, on a water-bath to about 1 or 2 ml., and allowing the residue to cool.

In Table I are recorded the results obtained in this test with varying quantities of neutral solutions of para-acid, salicylic acid and mixtures of the two. There was no difficulty in obtaining the crystals when para-acid alone was present. The presence of copper salicylate definitely increased the time required by the copper *p*-hydroxybenzoate for crystallisation.

TABLE I

Volume of ammonium *p*-hydroxybenzoate solution (1 ml. = 1 mg. of acid) ml.	Volume of ammonium salicylate solution (1 ml. = 1 mg. of acid) ml.	Results
2	Nil	Crystals in less than 30 minutes
5	,,	,, ,, ,, ,, 15 ,,
10	,,	,, ,, ,, ,, 15 ,,
20	,,	,, ,, ,, ,, 10 ,,
Nil	2	No crystals in 24 hours
,,	5	,, ,, ,, ,, ,,
,,	10	,, ,, ,, ,, ,,
,,	20	,, ,, ,, ,, ,,
2	2	Crystals in 2 hours
2	5	No crystals in 5 hours, but definite crystals in 15 hours
5	5	Crystals within 30 minutes
10	10	,, ,, 30 ,,

This test we consider very important because it is the only one, in our experience, which will definitely prove the presence of para-acid. It should be applied whenever Millon's test is positive. If the characteristic crystals are not formed within 10 or 12 hours the absence of para-acid may be inferred, whereas their formation is a direct proof of its presence, whether or no salicylic acid be also present.

V. NICHOLLS'S TEST.—This test (*cf.* p. 174), like Mohler's test (*infra*), is of use for the detection of benzoic acid in presence of both salicylic and para-acids. If salicylic acid is proved absent by tests II and III, a positive Nicholls test proves the presence of benzoic acid. If salicylic acid is also present, this test should be applied after destruction of the salicylic acid with alkaline permanganate. Alternatively, Mohler's test may be applied without removal of salicylic acid for the mere *detection* of benzoic acid. In *determining* this acid, however, by either Nicholls's test or Mohler's test, salicylic acid must be destroyed; para-acid does not interfere in Nicholls's test.

VI. MOHLER'S TEST.—In applying this test the neutral solution of ammonium salt is evaporated to dryness with 0·1 N potassium hydroxide solution in quantity just sufficient to form the potassium salt; the details as described by Illing (*loc. cit.*) are then followed. Benzoic acid gives a red colour, salicylic acid a yellow to brownish-yellow, whilst para-acid gives no colour.

The results of Tests I–VI are summarised in Table II.

It will be noticed that these tests will readily distinguish between salicylic acid and para-acid when they occur separately. Also, it is quite easy, by applying tests II and III to detect and determine salicylic acid in presence of para-acid;

TABLE II

Tests	Para-acid	Salicylic acid	Benzoic acid
I. Millon	Rose-red colour	Orange-red colour	No colour
II. Ferric chloride	No colour (see observations on p. 179)	Violet colour	„ „
III. Jorissen	Yellowish colour	Pink colour	„ „
IV. Copper crystals	Characteristic crystals	No crystals	——
V. Nicholls (as modified)	No colour	——	Violet colour due to formation of salicylic acid
VI. Mohler (as modified by Illing)	„ „	Yellow to brownish-yellow colour	Red colour

but the converse, the detection (and more so the determination) of para-acid in presence of salicylic acid is relatively difficult. In addition to the copper-salt test, a good indirect indication of para-acid in presence of salicylic acid may be obtained as follows:

VII. INDIRECT TEST.—The exact amount of salicylic acid in, say, 20 ml. of the neutral solution of ammonium salts is first determined by test II or III. A fresh 20-ml. portion and a standard containing this amount of salicylic acid in 20 ml. of water are taken for the Millon test. The colours obtained are compared in Nessler glasses after dilution to 50 ml.

In the absence of para-acid the two colours will match well, but if any appreciable quantity of that acid is present the two tints will be different, the test solution being more rose-red than the standard. We have actually made use of this indirect test to determine para-acid in presence of salicylic acid (p. 184).

The scheme shown in Table III will be found useful for the detection of these preservatives when present separately or together in foods, all the tests being carried out on aliquot portions of the neutral solution of the ammonium salts.

TABLE III

Test	Result	Inference	Remarks
I. Millon	No red colour	Salicylic and para-acids absent	Omit tests II, III, and IV
	Red colour	Salicylic and/or para-acid present	Apply tests II, III, and IV
II. Ferric chloride	Violet colour	(*a*) Salicylic acid present (*b*) Para-acid may also be present	Confirm by test III In either case confirm by test IV
	No violet colour	(*a*) Para-acid alone may be present (*b*) Salicylic acid absent	Omit test III
III. Jorissen	Pink colour	Confirms presence of salicylic acid	
IV. Copper salt	Characteristic crystalline precipitate	Confirms presence of para-acid	
	No crystals within 12 hours	Para-acid absent	
V. Nicholls*	No violet colour	Benzoic acid absent	
	Violet colour	Benzoic acid present	Confirm by test VI
VI. Mohler as modified by Illing	Red colour	Confirms presence of benzoic acid	

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* If tests II and III are positive, the preliminary oxidation with alkaline permanganate must be carried out before applying this test.

APPROXIMATE DETERMINATION OF PARA-ACID AND ITS DERIVATIVES IN FOODS

(A) IN ABSENCE OF SALICYLIC ACID.—The rose-red colour produced by para-acid with Millon's reagent is directly proportional to the amount of the acid present and can be utilised for its approximate determination as follows:—Twenty ml. of the neutral solution of the ammonium salt, obtained as described later, containing not more than 2·0 mg. of para-acid,* are treated in a boiling-tube with 2 ml. of Millon's reagent. A series of standards containing 1, 2·5, 5, 7·5, and 10 ml., etc., of an aqueous solution of para-acid (1 ml. = 0·1 mg.) diluted to 20 ml. with water, is prepared in boiling-tubes, and 2 ml. of Millon's reagent are added to each. The test solution and the standards are heated in a boiling water-bath for *exactly* two minutes, and then diluted immediately to 50 ml. in Nessler glasses, and the colours are compared. This determination can be repeated with the quantity of the standard indicated by this preliminary determination so as to obtain a more accurate figure.

Milk.—Ten mg. of the ethyl ester (solution in alcohol) were added to 25 ml. of milk. The milk containing the preservative was treated in a 50-ml. measuring flask, with two 5-ml. portions of phosphotungstic acid reagent,† or 5 ml. of zinc acetate solution,† followed by 5 ml. of potassium ferrocyanide† solution. The mixture was diluted to 50 ml., well shaken, and after about 5 minutes filtered through a dry paper, and 30 ml. of the filtrate were collected. This was saturated with ammonium sulphate and extracted three times with 15-ml. portions of ether, the ethereal extracts being collected in a flask and the ether removed. To the residue 60 ml. of alcohol and 5 ml. of 0·5 *N* alcoholic potash were added, and the mixture was refluxed on a water-bath for two hours. The bulk of the alcohol was then removed by evaporation, and the residue was diluted with water, acidified with dilute sulphuric acid and extracted three times with 15-ml. portions of ether after saturation with ammonium sulphate. The mixed ethereal extracts were shaken three times with 10-ml. portions of 10 per cent. ammonia solution, the mixed ammoniacal extracts were transferred to a conical flask, and the excess ammonia was removed by boiling until the vapours were quite neutral. The neutral solution was cooled and diluted to 100 ml., and 20 ml. were taken for determination with Millon's reagent.

The average recovery of ethyl ester in our experiments with milk was 60 per cent.

Cordials.—Ten mg. of ethyl ester were added to 20 ml. of the cordial. The sample was directly extracted with three successive quantities of 15 ml. of ether after acidifying with dilute sulphuric acid and saturating with ammonium sulphate. After removal of the ether the hydrolysis with alcoholic potash and the conversion of the free acid thus obtained into its ammonium salt were carried out as described under milk, the cooled neutral solution was diluted to 100 ml., and 20 ml. were taken for determination as before.

The recovery of the ester was usually about 90 per cent.

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* It was found difficult to obtain a good match when the quantity of para-acid exceeded 2·0 mg.

† These precipitants were prepared exactly as described in the Second Report of the Milk Products Sub-Committee.[8]

In applying the test to alcoholic wines, the alcohol should be removed as far as possible by evaporation before extraction with ether.

Fatty Foods and Meat and Fish Products.—The free acid and its esters are very soluble in alcohol, but only moderately soluble in fats and oils. It was therefore found possible to extract them readily by boiling with successive quantities of alcohol as described hereunder.

Butter.—Ten mg. of the ethyl ester (in solution in alcohol) were thoroughly mixed with 25 g. of the melted butter, and the mixed sample was boiled in a conical flask on the water-bath for thirty minutes with 100 ml. of alcohol, with occasional shaking. The mixture was cooled thoroughly under the tap to let the fat almost solidify and then filtered, and the residue in the flask was washed with two or three successive portions (20 ml.) of boiling alcohol and each time cooled again and filtered. To the mixed alcoholic filtrates 20 ml. of 0·5 N alcoholic potash were added, and the subsequent stages of the process were carried out exactly as described for milk. The neutral solution of ammonium salt was diluted to 100 ml., and 20 ml. were taken for the determination.

In working with fatty substances small quantities of free fatty acids are also extracted, and these naturally persist up to the last stage, even making the neutral extract slightly turbid when the excess ammonia is completely removed. These fatty acids, however, are precipitated on addition of Millon's reagent; if they are filtered off, the determination can be continued by heating the filtrate as usual for two minutes and then matching the colours.

The recovery of ethyl ester attained with butter, etc., was usually over 90 per cent.

Sausage.—Ten mg. of the ethyl ester were well mixed with 25 g. of sausage, and the mixed sample was boiled in a conical flask for thirty minutes with 100 ml. of alcohol, with repeated shaking. The mixture was allowed to settle for a minute or two and filtered hot through a Buchner funnel containing a pad of cotton-wool on the top of the filter-paper. The residue in the flask was washed with hot alcohol two or three times and filtered. The alcoholic filtrate obtained was slightly turbid, possibly because of the presence of a little fat or starchy matter which unavoidably filtered through. This did not interfere with the hydrolysis, which was carried out as usual after adding 20 ml. of 0·5 N alcoholic potash, and the determination was completed as before. The ammonium salt solution, which was diluted to 100 ml., was again somewhat turbid, as with butter. The same procedure of adding 2 ml. of Millon's reagent to 20 ml., filtering and heating the filtrate in a boiling water-bath, was adopted.

The recovery of ester from sausage and similar foods was found to be of the order of 84 per cent.

The method adopted for sausage is also applicable to minced meat, meat and fish pastes, tinned fish, and similar articles.

The procedure of isolating the preservatives from various foods, as described above, by hydrolysis of the esters is advantageous for two or three reasons. First, para-acid and its esters are often used in admixture with one another, and the identification and determination of the different esters separately through the particular alcohols produced (*cf.* Weiss[3]) is not only lengthy and tedious, but is also unnecessary, at any rate in food work in this country. It is sufficient to return results as "a preparation of para-hydroxybenzoic acid equivalent to *x* parts of para-hydroxybenzoic acid per million." Secondly, the reaction of the free acid with Millon's reagent is quicker and more delicate than that of the esters, and the red colour is also deeper. Thirdly, the important and decisive copper-salt test can be applied only to the free acid or its neutral salts.

(B) IN PRESENCE OF SALICYLIC ACID.—The exact determination of the amount of para-acid in presence of salicylic acid is a matter of some difficulty. We attempted to separate the two quantitatively through their copper-salts, using different solvents, such as 50 per cent. alcohol, acetone, etc., but without success.

In the preliminary experiments we observed that with Millon's reagent the two acids give a reddish colour of equal depth, but of different shades, and that a good estimate of the proportion of the one to the other could be arrived at by comparing with a series of mixed standards as follows:

The exact amount of salicylic acid is first determined in the neutral extract of the mixed ammonium salts by tests II or III. The volume of this solution is then adjusted to contain 0·5 mg. of salicylic acid in 20 ml., this volume being taken for the Millon test. A series of mixed standards is prepared in which the proportions of salicylic acid (the amount of which is kept constant) to para-acid in the 20 ml. are 0·5 : 0·1, 0·5 : 0·25, 0·5 : 0·5, 0·5 : 0·75, 0·5 : 1·0, and so on, all in mg. in 20 ml. It is, of course, not essential to adjust the concentration to contain 0·5 mg. of salicylic acid in 20 ml. of the neutral solution of the mixed ammonium salts so long as this concentration is not exceeded. This is merely a convenient dilution, and any weaker one may be chosen, but it is essential that the exact quantity of salicylic acid be known. If, for instance, the dilution is such that 20 ml. contains only 0·2 mg. of salicylic acid, all the mixed standards should be made to contain this amount of salicylic acid, whilst the quantities of para-acid are varied as above.

The tests are completed as described, and it will usually be found possible to estimate the relative proportions with a fair degree of accuracy.

The method is illustrated by the following experiments. A cordial containing 0·025 per cent. of salicylic acid and 0·025 per cent. of para-acid was prepared. The mixed acids were isolated as usual as their ammonium salts, and this solution was diluted to 1000 ml., so that 20 ml. taken for the test contained 0·5 mg. of salicylic acid. Mixed standards were prepared in which the proportions of salicylic acid to para-acid were (*a*) 0·5 : 0·3, (*b*) 0·5 : 0·4, (*c*) 0·5 : 0·5, (*d*) 0·5 : 0·6, and (*e*) 0·5 : 0·7 —all in mg. in 20 ml. The tests were completed as usual. The colour obtained with the test solution was markedly different from those in standards (*a*), (*d*) and (*e*), but it was a little difficult to decide whether it matched (*b*) more closely than (*c*), thus indicating that the proportions were almost equal.

In certifying adulteration when indications are obtained that both these acids are present together, it is perhaps advisable to return the results as "a preparation of hydroxybenzoic acid equivalent to *x* parts of hydroxybenzoic acid per million" without giving the proportions of the two isomers found.

We are indebted to Mr. J. R. Nicholls, of the Government Laboratory, for some useful suggestions and for his valued criticism. We also wish to thank

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ROYAL DENTAL HOSPITAL
LEICESTER SQUARE, W.C.2

The Use of Hexamine for the Separation of Thorium from the Rare Earths, and its application to the Determination of Thorium in Monazite Sand

BY A. M. ISMAIL, PH.D., AND H. F. HARWOOD, M.SC., PH.D., F.I.C.

HEXAMINE (hexamethylenetetramine) has been used by various workers as a precipitant for certain metallic radicles; it was employed by Kollo[1] in the separation of iron from manganese, and Kollo and Georgian[2] extended its use to the separation of aluminium from calcium, recommending it in place of ammonia. They explained the mechanism of the reaction which takes place when hexamine is used as a precipitant, pointing out that it decomposes when boiled with the salt solution, ammonia being formed.

Rây and Chattopadhya[3] described hexamine as a reagent which effects a quantitative separation of ferric iron from zinc, cobalt, nickel and manganese. They gave a thorough and clear explanation of the reaction involved, and showed also that this reagent will precipitate aluminium, titanium and thorium. Rây[4] extended the application of hexamine as an analytical reagent to the determination of the metals of the ammonium hydroxide group in the presence of manganese, nickel, cobalt and magnesium. Hexamine precipitates quantitatively the hydroxides of ferric iron, aluminium, chromium, titanium, uranium, zirconium and thorium, but in the presence of ammonium salts, zinc, manganese, nickel, cobalt and magnesium remain in solution. The method given permits of the quantitative separation of iron from all the last-mentioned bivalent metals; aluminium is readily separated from all except nickel, although the separation from large quantities of zinc is incomplete. The separation of titanium is quantitative except when large amounts of zinc are present, and the separation of uranium presents no difficulties. A separation of zirconium and thorium from the bivalent metals of the ammonium sulphide group can also be effected by hexamine.

Rây examined the behaviour of hexamine towards solutions of the salts of the rare earths. Lanthanum, cerium, praseodymium, neodymium, and yttrium gave no precipitate in the cold, but on heating the solution to boiling a faint turbidity formed; the addition of ammonium salts completely prevented this. No separation of the rare earths from manganese, cobalt, nickel and zinc could be effected with hexamine, neither did Rây examine the possibility of a separation of thorium from the rare earths with this reagent.

THE HEXAMINE METHOD FOR THE SEPARATION OF THORIUM FROM THE RARE EARTHS.—The following table (due to Britton[5]) gives the hydrogen ion concentrations at which certain hydroxides are precipitated.

	*p*H		*p*H
Magnesium ..	10·5	Lead	6·0
Silver	9 (?)	Beryllium	5·7
Manganese	8·5–8·8	Iron (ous)	5·5
Lanthanum ..	8·4	Copper (ic)	5·3
Cerium (ous) ..	7·4	Chromium	5·3
Mercuric	7·3	Zinc	5·2
Praseodymium ..	7·1	Uranium	4·2
Neodymium ..	7·0	Aluminium ..	4·1
Samarium	6·8	Thorium	3·5
Cobalt	6·8	Tin (ous)	2 (?)
Yttrium	6·8	Zirconium	2 (?)
Cadmium	6·7	Iron (ic)	2 (?)
Nickel	6·7		

The great difference in the hydrogen ion concentrations accounts for the ease with which thorium can be separated from the rare earths by methods depending on the change in *p*H. Reagents which have been used for controlling the hydrogen ion concentration in such a separation are sodium thiosulphate and sodium azide; a separation can also be effected by hexamine. This latter substance is an exceedingly weak base, and its aqueous solution has a neutral reaction to litmus. In the presence of hydrogen ions it is hydrolysed into formaldehyde and ammonia, the hydrogen ions formed through the hydrolysis of salts already in the solution being frequently enough for the decomposition of the hexamine to proceed. The hydrolysis of thorium salts in solution is sufficiently great to cause the precipitation of thorium hydroxide on the addition of hexamine, even in the presence of ammonium salts which lower the hydroxyl ion concentration of the ammonium hydroxide produced from the hexamine. On the other hand, the precipitation of the hydroxides of cerium, lanthanum, yttrium, etc., by hexamine is completely prevented by the presence of ammonium salts, even if the solution is heated to boiling.

The following Tables, A to F, give the results obtained in the course of investigations made to ascertain the best conditions for separating thorium from cerium (and the other rare earths) by means of hexamine. The thorium and cerium nitrates used in these experiments were of a high grade of purity. Stock solutions of the two salts were prepared, and standardised carefully by precipitation with (*a*) oxalic acid, and (*b*) ammonia.

The salts of lanthanum, praseodymium, neodymium, and yttrium used in some of the experiments were also the purest obtainable nitrates that could be purchased.

In the course of the actual determinations the precipitates of thorium hydroxide obtained in the separation were ignited directly to oxide, and the cerium in the filtrate was precipitated by the addition of ammonia (together with a few drops of hydrogen peroxide when lanthanum was present), the precipitate being ignited and weighed as the oxide.

SEPARATION OF THORIUM FROM CERIUM

TABLE A

Weight of ammonium chloride added, 5 g.
Volume of solution 100 ml.
Temperature 30°.
The precipitant (hexamine) was added rapidly, and only a single precipitation was made.

ThO_2 used g.	CeO_2 used g.	CeO_2 found g.	Difference	ThO_2 found g.	Difference g.
0·0420	0·0370	0·0371	+0·0001	0·0419	−0·0001
0·0420	0·0370	0·0365	−0·0005	0·0420	Nil
0·0420	0·0185	n.d.	—	0·0421	+0·0001
0·0420	0·0093	0·0090	−0·0003	0·0424	+0·0004
0·0420	0·0047	0·0045	−0·0002	0·0420	Nil
0·0210	0·0370	0·0369	−0·0001	0·0212	+0·0002
0·0105	0·0370	0·0367	−0·0003	0·0109	+0·0004
0·0027	0·0370	0·0352	−0·0018	0·0038	+0·0011
0·0027	0·0370	0·0362	−0·0008	0·0035	+0·0008

TABLE B

Weight of ammonium chloride added, 5 g.
Volume of solution 100 ml.
Temperature 30°.
The precipitant was added, drop by drop, with continual stirring of the solution, and only a single precipitation was made.

ThO_2 used g.	CeO_2 used g.	CeO_2 found g.	Difference	ThO_2 found g.	Difference g.
0·0076	0·0370	0·0362	−0·0008	0·0085	+0·0009
0·0076	0·0370	n.d.	—	0·0077	+0·0001
0·0050	0·0370	0·0361	−0·0009	0·0064	+0·0014
0·0050	0·0370	n.d.	—	0·0055	+0·0005
0·0027	0·0370	0·0362	−0·0008	0·0036	+0·0009
0·0027	0·0370	0·0367	−0·0003	0·0037	+0·0010

The results in Tables A and B show a slight positive error in the figure for the thoria, more especially when the amount of cerium present is greatly in excess of that of the thorium. A further set of determinations was then carried out in which the thorium precipitate first obtained was re-dissolved, and the precipitation with hexamine was repeated. As is evident from the figures in Table C, this procedure effects a perfectly satisfactory separation, even when a very large excess of cerium is present.

TABLE C

Conditions as in B, except that a double precipitation of the thorium was made.

ThO_2 used g.	CeO_2 used g.	CeO_2 found g.	Difference	ThO_2 found g.	Difference g.
0·0076	0·0370	0·0370	Nil	0·0076	Nil
0·0050	0·0370	0·0369	−0·0001	0·0050	Nil
0·0027	0·0370	0·0368	−0·0002	0·0026	−0·0001

SEPARATION OF THORIUM FROM LANTHANUM, NEODYMIUM, PRASEODYMIUM, AND YTTRIUM

TABLE D

Conditions as in C.

ThO_2 used g	Rare earth oxides used, g	ThO_2 found g.	Difference g.
0·0420	0·242 Ce, La, Nd, Pr, Y	0·0427	+0·0007
0·0420	0·242 ,, ,,	0·0426	+0·0006
0·0420	0·040 La oxide	0·0421	+0·0001
0·0420	0·040 Pr oxide	0·0421	+0·0001
0·0420	0·040 Nd oxide	0·0422	+0·0002
0·0420	0·040 Y oxide	0·0424	+0·0004

TABLE E

Conditions as in D, except that after a double precipitation of the thorium with hexamine, the hydroxide was re-dissolved, and the thoria was precipitated as oxalate, ignited and weighed.

ThO_2 used g.	Rare earth oxides used, g.	ThO_2 found g.	Difference g.
0·0420	0·040 Y oxide	0·0420	Nil
0·0420	0·040 Nd oxide	0·0419	−0·0001
0·0420	0·242 Ce, La, Nd, Pr, Y oxides	0·0420	Nil
0·0420	0·242 ,, ,,	0·0420	Nil

In the two following determinations the thorium and rare earths were first precipitated with oxalic acid, the oxalates were ignited, the oxides were dissolved in hydrochloric acid, and the thorium was separated as before by a double precipitation with hexamine, ignited to oxide and weighed.

ThO_2 used g.	Rare earth oxides used, g.	ThO_2 found g.	Difference g.
0·0420	0·242 Ce, La, Nd, Pr, Y	0·0421	+0·0001
0·0420	0·242 ,, ,,	0·0420	Nil

The method finally adopted for the precipitation of thorium by hexamine in the presence of cerium and other rare earths is as follows:—The faintly acid solution of the metals, which should have a volume of 100 ml., is warmed to 30° C., and 5 g. of ammonium chloride are added. A 10 per cent. solution of hexamine is then added, drop by drop, with stirring after each addition, until a slight excess is present. The precipitate of thorium hydroxide is allowed to settle, the liquid is decanted through a Whatman No. 41 filter, and the precipitate is finally transferred to the paper and washed with warm 2 per cent. ammonium nitrate solution. The precipitate is then dissolved on the filter with hot 2 *N* hydrochloric acid, and the paper is well washed with hot water. The solution is diluted if necessary, neutralised with ammonia, and made faintly acid to methyl red with hydrochloric acid. Sufficient ammonium chloride is then added to bring its content in the solution up to 5 per cent., the solution is warmed, and the thorium is precipitated as before. The washed precipitate is ignited and weighed as ThO_2.

The cerium in the united filtrates is precipitated by the addition of a slight excess of ammonia and a few drops of 6 per cent. hydrogen peroxide to the hot solution, the liquid being then boiled for 2 minutes, and the precipitate of cerium hydroxide filtered off, washed with hot 2 per cent. ammonium nitrate solution, ignited and weighed.

In the majority of cases a single precipitation of the thorium suffices to give a satisfactory separation, but if the greatest accuracy is required, and especially if the amount of cerium present preponderates greatly over the thorium, a double precipitation, as described above, is advisable.

APPLICATION OF THE METHOD TO THE DETERMINATION OF THORIA IN MONAZITE SAND.—Five g. of the sand, ground to a fine powder, are weighed into a platinum dish, and sulphuric acid (about 25 ml.) is added so as to produce a stiffish paste. The dish is then covered and heated at 150–180° C. for four hours, with frequent stirring. After cooling, the contents of the dish are added to about 180 ml. of water at 0° C., in small portions at a time, and with constant stirring. The beaker is kept immersed in ice-water to maintain the temperature at 0° C. during solution. The pasty mass dissolves completely, with the exception of a small residue composed chiefly of zirconium and silicon compounds. The dish is then well rinsed out with cold water, and the whole is well mixed and allowed to stand for some hours, or preferably overnight. The solution is filtered into a 250-ml. graduated flask, the residue and filter are well washed with cold water acidified with sulphuric acid, and the solution is diluted to the mark and well mixed. Fifty ml., representing 1 g. of the original sand, are pipetted into a 150-ml. beaker and nearly neutralised with ammonia, concentrated ammonia being used at first, and a dilute solution towards the end of the neutralisation; 1·5 ml. of conc. hydrochloric acid are quickly added, the solution is diluted to 70 ml. and heated to 60° C., and then 30 ml. of a cold, saturated solution of oxalic acid are added, drop by drop, with vigorous stirring. The whole is kept at 60° C. for one hour, then well stirred and allowed to stand overnight. The liquid is decanted through a Whatman No. 40 filter, and the precipitate is transferred to the paper and washed with a warm solution containing 2 per cent. of oxalic acid and 0·1 per cent. of hydrochloric acid; the oxalates are then ignited to convert them into oxides.

The ignited oxides are transferred to a beaker, and the crucible is rinsed well with dilute (1 : 1) hydrochloric acid. Ten ml. of this acid are poured into the crucible, which is then heated on a water-bath to dissolve any traces of oxide adhering to the walls. The resulting solution is added to that already in the beaker, and more acid is introduced until the total volume of liquid is about 50 ml.; finally, 10 drops of 6 per cent. hydrogen peroxide are added. The covered beaker is heated with a small flame, so that the liquid is kept just below the boiling-point. Complete solution of the oxides is attained after about two hours.

The clear solution of the chlorides is evaporated to dryness, 1·5 ml. of hydrochloric acid are added, the residue is taken up with water, and the solution is diluted to 50 ml. The whole is heated to 60° C., and the rare earths are again precipitated by the addition of 25 ml. of oxalic acid solution. The precipitate is filtered off, washed, ignited and weighed. It is then dissolved in hydrochloric acid as before, the solution is again evaporated to dryness, and the residue is moistened with two drops of hydrochloric acid. Water is then added, and the solution is diluted to 100 ml.; the thorium present can then be separated and determined by the hexamine method previously described.*

The following table shows the results obtained in the analysis of a number of samples of monazite sand† by the hexamine method. As a check, the thorium content of three of the samples was also determined by the standard thiosulphate method. As will be seen from the table, the agreement between the two sets of figures obtained is perfectly satisfactory. The separation of thorium from the rare earths by the thiosulphate method, although yielding good results, is tedious and requires considerable time. Re-precipitation of the thoria more than once is necessary, in order to effect a complete separation, whilst, on the other hand, the filtrates obtained in the process must all be worked up to recover the traces of thoria which they contain, with considerable expenditure of time. A further drawback is the separation of sulphur during the boiling of the solution with sodium thiosulphate, and the consequent impossibility of telling whether any precipitation of thoria has taken place, especially when small amounts of this element are in question.

The hexamine method gives a sharp separation of the thoria after two precipitations with the reagent, and effects a considerable saving of time, as the precipitate of thorium hydroxide is readily filtered off and washed, and no re-working of the filtrates is necessary, as in the thiosulphate method.

DETERMINATION OF THORIUM IN MONAZITE SAND

Sample	Hexamine method Thorium dioxide, per cent.	Thiosulphate method Thorium dioxide, per cent.
1	7·32	7·30
	7·40	7·38
2	7·85	7·83
	—	7·89
3	9·10	—
	9·20	—
4	10·04	—
	10·08	—
	10·07	—
5	9·76	9·83
	9·77	9·78

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* In order to ensure complete precipitation of the rare earth oxalates the amount of rare earth oxides present in 100 ml. of solution should not be less than 1 g.

The sulphuric acid solution of the sand should be carefully neutralised by adding the dilute ammonia, drop by drop, stopping the addition before a faint permanent turbidity is produced; the hydrochloric acid is then quickly added. The solution should be clear, and remain so when heated to 60° C. If the neutralisation is carried out as described, a second oxalate precipitation of the rare earths will frequently prove unnecessary.

† Most of the samples used were kindly furnished by Mr. S. J. Johnstone, of the Imperial Institute, and Mr. H. F. V. Little, of Thorium, Ltd., to whom we wish to express our thanks.

Summary.—Thorium can be quantitatively separated from cerium and other rare earths by using hexamine as a precipitant. The application of the method to the determination of thorium dioxide in monazite sand is described.

References

1. C. Kollo, *Bul. Soc. Chim. Rumania*, 1920, **2**, 89.
2. C. Kollo and N. Georgian, *Ibid.*, 1924, **6**, 111.
3. P. Rây and A. K. Chattopadhya, *Z. anorg. Chem.*, 1928, **169**, 99.
4. P. Rây, *Z. anal. Chem.*, 1931, **86**, 13.
5. H. S. Britton, *J. Chem. Soc.*, 1925, **127**, 2142.

Imperial College of Science
and Technology
South Kensington, S.W.7

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF ANTIMONY IN LEAD-RICH ALLOYS

Having frequent occasion to determine antimony in lead-rich alloys for the purpose of works control, I read with much interest the paper by K. Stanford and D. C. M. Adamson in the January Analyst.

The method employed here is a modification of that described by Low in his textbook (*Technical Methods of Ore Analysis*, 1927, p. 296).

A one-gram sample in a 500 ml. Pyrex conical flask is digested with 10 ml. of conc. sulphuric acid, to which is added about 5 g. of anhydrous sodium sulphate. The flask is held in Fisher tongs over the flame of a large Bunsen burner, and a few minutes' vigorous boiling suffices to produce an almost white melt. When cool, this is gently warmed with 30 ml. of water and 20 ml. of hydrochloric acid until the sodium salts are in solution, when the contents are briskly boiled for 30 seconds. Eighty ml. of water are then added, the flask is cooled to below 20° C., and the solution is titrated in the usual way with permanganate solution which is equivalent to approximately 0·01 g. of antimony per ml.

The advantages of a conical flask over a crucible for the attack are obvious, especially when many samples have to be analysed, and anhydrous sodium sulphate is an innocuous reagent which is more conveniently handled than the bisulphate.

No trouble is met with from adsorption of antimony, but, under these conditions, the titration is not strictly proportional in presence of lead, slightly more permanganate being required than for the same weight of antimony alone. Tables I and II, in the paper under discussion, support this observation by showing a tendency towards a negative error in the absence, and a positive error in the presence, of lead.

In my experience, the magnitude of the error is dependent upon the relative proportions of antimony and lead present. Presumably lead, by virtue of the fact that the final solution is saturated, may be regarded as constant in amount when it is the major constituent. The error, which may amount to 0·10 ml. or 0·1 per cent. on an alloy containing 10 per cent. of antimony, may be made negligible by standardisation with similar proportions and amounts of the two metals.

R. G. Robinson

Britannia Lead Co., Ltd.
Northfleet, Kent

THE DEVELOPMENT OF LATENT FINGER-PRINTS WITH DYESTUFFS

In the course of his lecture to the Manchester Section of the Institute of Chemistry, on January 14th, Dr. Ainsworth Mitchell mentioned that he had used various dyes, notably methylene blue, for the development of latent finger-prints on documents, but that the method had the drawback that the developed prints were readily smudged.

As a result of the discussion on this point, I have made a number of experiments with basic dyestuffs and find that Victoria Blue BS is satisfactory for the purpose. In these experiments the cleaned fingers, thumbs and, in one instance, the whole hand, were pressed on to white cardboard, and the basic dyestuff in powder form was dusted over the cardboard. Basic dyestuffs have the property of being readily absorbed by grease, and therefore clearly showed up the ridges where grease had been transferred from the fingers and thumb on to the card. In order to fix the dyestuff, the cards were held for a few minutes over boiling 30 per cent. aqueous acetic acid solution, the fixation being effected by acetic acid vapour and steam. In this way positives are obtained, and should be suitable for photographing. The finger-prints on the cards thus obtained should also be quite durable if kept in the dark. Basic dyestuffs, however, are rather fugitive to light.

H. A. Thomas

Imperial Chemical Industries, Ltd.
(Dyestuffs Group)
Hexagon House
Blackley, Manchester

OPTICAL ACTIVITY OF PREPARATIONS OF SQUILLS

Of several samples of Acetum Scillae and Tinct. Scillae examined in this Laboratory, all have been found to possess a marked degree of optical activity (laevo-rotatory).

These observations were made during an investigation carried out to determine the reason why samples of Oxymel Scillae B.P., 1932, failed repeatedly to pass the test for optical rotation, invariably giving a reading in excess of the B.P. limit of $-1{\cdot}9$ for a 25 per cent. w/v solution.

It would appear that the B.P. limits for the optical rotation of Oxymel Scillae had been drawn up on the assumption that only the honey present contributed to the optical activity of the preparation.

It seems necessary, in the light of the foregoing observations, that the optical activity of the Acetum Scillae used in making Oxymel Scillae should also be taken into account in calculating the official limits for optical rotation, and that the limiting figure should be considerably higher on the laevo side than at present.

Leo McGraghan

Analytical Laboratory
Messrs. Brady & Martin, Ltd.
Newcastle upon Tyne

Official Appointments

THE Minister of Health has approved the following appointments:

REGINALD FRANK WRIGHT as a Public Analyst for the County Borough of Eastbourne, in addition to S. Allinson Woodhead (November 10th, 1936).

REGINALD FRANK WRIGHT as a Public Analyst for the Borough of Hove, in addition to S. Allinson Woodhead (November 26th, 1936).

ARTHUR EDGCOME BROWN as additional Public Analyst for the Metropolitan Borough of Deptford from January 1st, 1937, in addition to Hugh Amphlett Williams, who becomes Senior Public Analyst from April 1st, 1937. H. G. Harrison retired March 31st, 1937 (January 6th, 1937).

ERIC VOELCKER as a Public Analyst for the Borough of Chipping Wycombe in place of B. H. Gerrans (deceased) (January 6th, 1937).

HUGH AMPHLETT WILLIAMS as Additional Public Analyst for the Metropolitan Borough of Greenwich, in addition to A. E. Brown (January 6th, 1937).

Department of Scientific and Industrial Research

FOOD INVESTIGATION. Special Report No. 44

SECOND REPORT ON THE CORROSION OF THE TIN-PLATE CONTAINERS BY FOOD PRODUCTS*

IN the First Report on this subject (*cf.* ANALYST, 1931, **56**, 315) the methods of preventing or mitigating the corrosion of tin-plate containers were discussed. Since then considerable advances have been made in lacquers and methods of applying them. The drawback of the custom of lacquering the flat sheet and fashioning and soldering the bodies after stoving is that some damage to the can is bound to occur. To remedy this, attempts have been made in U.S.A. to spray finished cans with a further coating of lacquer of a type that would require only a short stoving. If satisfactory synthetic lacquers can be developed that need stoving for only 10 or 20 minutes, or even less, it may become possible to abolish lacquering on the flat.

ALTERNATIVES TO TIN-PLATE.—Glass now used is highly resistant to blows and changes of temperature, and rapid mechanical handling, filling and hermetic sealing with metal caps may reduce the cost almost to that of tin-plate.

Aluminium.—The use of aluminium cans for fish products is increasing, especially in Norway. Aluminium does not blacken when used with crustacea, etc., nor bring about in fish products those slow changes (darkening, etc.) that have been associated with traces of iron derived from the can. Aluminium cans have not, so far, proved successful with tomato, fruits, etc., owing to the rapid formation of hydrogen-swells. Moreover, aluminium plate is not so strong as tin-plate and is more difficult to make into cans, so that it is unlikely to come into general use.

THE CORROSION OF TIN.—Except for special purposes, the general methods of research and the apparatus previously used have been little modified. As before, citric acid (0·5 to 1 per cent.) has for the most part been used as the basal corroding medium, with sodium citrate as a buffer to give a *p*H-range from about 2·4 to 5·5.

Specimens of steel and tin for the immersion tests have been prepared by treatment with emery cloth and by degreasing with benzene and other solvents. Specimens of tin-plate have also been treated with emery to remove a definite area of the tin, thus forming a convenient tin-iron couple for immersion tests, the technique being as follows:—The specimen is first degreased, and the portion to be left intact is coated with paraffin wax. The portion to be de-tinned is then immersed in Clarke's reagent (ANALYST, 1934, **59**, 525) until one minute after the evolution of gas has ceased. All the tin is thus removed, together with the greater part of the tin present in the tin-iron compound. The wax is then dissolved off, and the specimen is clamped in a frame that protects the tinned portion, while the bare portion is treated with emery to obtain the standard surface.

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* By T. N. Morris, M.A., and J. M. Bryan, B.Sc., Ph.D. London: H.M. Stationery Office. Price 1s. net.

Effect of Ferrous Iron.—Experiments in which the *p*H was varied or kept constant showed that the concentration of stannous tin is at a maximum at *p*H 3, whilst stannic tin predominates at *p*H 4 to 5·5. In other words, during the early stages of corrosion oxygen is more efficient quantitatively as a corroding agent for tin in the presence of ferrous iron at *p*H 3 than at any other point on the range. Increasing the concentration of iron in solution considerably increased the quantitative efficiency of oxygen as a corroding agent in the early stages of the test.

Effect of a Stannic Salt.—The presence of small quantities of a stannic salt had no apparent effect on the corrosion of tin over the range *p*H 2·4 to 5·5; hence a stannous salt would not act catalytically in promoting the corrosion of tin in presence of oxygen by alternate oxidation and reduction.

Effect of Copper.—Quantities of copper, up to 20 p.p.m. as citrate, were substituted for ferrous iron in the experiments. The results showed that the copper ion is not as effective as iron in accelerating the corrosion of tin in presence of air.

Sucrose.—Experience has shown that fruits packed in water give rise to fewer hydrogen-swells than fruits packed in syrup. It has been suggested that the explanation may be found in the presence of sulphur in the sugars used. In the experiments described the presence of sugar inhibited corrosion at 25° C. over the whole *p*H range, reducing it to one-third of the normal at *p*H 2·4, and to one-half at *p*H 5·5. Increasing quantities of sugar in the presence of 0·5 per cent. of citric acid at 25° C. progressively retarded the rate of corrosion of tin, probably owing to the progressive reduction of the solubility of air in the solutions. At 75° C. corrosion was stimulated, but this might have been due to products of the breakdown of the sugar, since considerable caramelisation occurred.

Sodium Chloride.—At 25° C. 1 per cent. of salt in presence of 0·5 per cent. of citric acid had no effect at *p*H 2·4, but from this point up to *p*H 5·5 there was a slight inhibiting effect on corrosion. At 75° C., with solutions containing 1 per cent. of citric acid, not buffered, and 2 per cent. of sodium chloride, the salt had an inhibiting effect.

Acids other than Citric Acid.—The hydroxy acids, lactic, tartaric and malic, had about the same corrosive powers as citric acid, but tin was not attacked by the non-hydroxy acids, acetic and succinic. This difference in behaviour towards tin finds a parallel in the behaviour of the respective sodium salts towards aluminium. Oxalic acid has strong corrosive powers, the metal becoming coated with an insoluble layer, probably tin oxalate. Phosphoric acid has little action; sulphuric acid proved less corrosive, and hydrochloric acid more corrosive than the hydroxy organic acids.

THE CORROSION OF MILD STEEL.—It has been suggested that the differences often found in the rate at which different specimens of steel and iron corrode under the same conditions may be due to variations in the amount of phosphorus in the steel; it is, however, quite as likely that sulphur in the steel is responsible; evidence in support of this is put forward in the Report.

The quality of steel must be considered in relation to the rate of diffusion of hydrogen through it, as well as to the velocity of corrosion. The formation of blisters is considered to be due to hydrogen assuming the gaseous form as inclusions or cavities in the steel. There is evidence that cold-rolling the steel sheet influences the rate of corrosion and results in a decreased tendency to the formation of hydrogen-swells; any factor improving the continuity of the tin coating will probably also improve that of the lacquer.

The Report also discusses the action of inhibitors and accelerators on the corrosion of mild steel, and experiments (described in detail) have been carried out on the corrosive action of various fruit juices.

Effect of Beet Sugar.—Commercial beet sugars commonly have an inhibiting effect on the corrosion of iron, and the favourable influence of adding a brown beet sugar to pure white sugar has been demonstrated in actual canning tests.

SULPHUR COMPOUNDS.—The effect of either sulphur dioxide or hydrogen sulphide in canning fruits of high acidity is to hasten the formation of hydrogen-swells.

THE TIN-IRON COUPLE AND TIN-PLATE.—In much of the work strips of tin-plate were adapted for a study of the tin-iron couple by laying bare definite proportions of the underlying steel. The following conclusions were drawn:

(i) In the absence of air, no matter what the relative areas of iron and tin may be, the corrosion of tin increases from *p*H 2 to *p*H 4, and sometimes beyond, while the corrosion of iron diminishes.

(ii) The presence of air increases the corrosion of tin, especially at high acidity.

(iii) Unless a very large proportion of tin is exposed, the corrosion of iron tends to be lower in the presence than in the absence of air, particularly at high acidity.

DISCOLORATION OF CANNED FRUITS.—Amounts up to 40 p.p.m. of aluminium, copper, nickel, chromium, zinc, lead and silver had no effect on the colour of fruits at room temperature or at 70° C. Strawberries are particularly sensitive to iron, 2 p.p.m. producing marked discoloration. With black currants, the greatest discoloration was produced by tin and the least by iron. Raspberries were only slightly discoloured by 10 p.p.m. of tin. The reason for the different behaviour of iron and tin lies in the fact that iron affects the tannins and allied substances derived from the seed-coats of the fruits, whilst tin affects the soluble anthocyanin pigments.

Queensland

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE, 1936

THE Acting Government Analyst (Mr. Frank E. Connah) reports that 13,6 samples were examined, as compared with 12,550 for the previous year. Of these, 6568 were for the Health Department, 2059 for the Customs and 345 for the Police. Among the points of interest to which special attention is directed are the following:

DIRT IN MILK.—The position with regard to visible dirt is fairly satisfactory. Very rarely does the weight of dirt in a sample exceed 1 grain per gall., but in sound dairy practice there should not be more than one-third of a grain. Under the pressure of modern dairy hygiene the old tolerance of 1·5 grain of visible dirt per gall. must be buried with an unclean past.

FORMALDEHYDE IN CURED FISH.—The Torry Research Station recorded some high formaldehyde results (about 10 p.p.m.) by Schryver's test on dry salt ling to which no formaldehyde had been added (ANALYST, 1936, 61, 340). Our experiments on tailer and mullet fish did not afford any evidence by this method of the presence of formaldehyde either in the fresh or salt-cured fish. Our reports on formaldehyde in fish have not been invalidated by the Torry Station investigation. Of 15 samples of cured fish examined, 14 contained formaldehyde in amounts ranging from 24 to 510 p.p.m. In some instances the odour of formaldehyde was pronounced. With imported moist lightly salted filleted haddock, only 4 p.p.m. was recorded.

LEAD IN PAINTS, CRAYONS AND TOYS.—Of 67 samples of paint examined, 45 contained more than 5 per cent. of soluble lead. Under the Queensland Health Acts no paint pigment may contain more than 5 per cent. of soluble lead, and soluble lead is determined, as in England,* by the method of Thorpe and Simmonds (*J. Chem. Soc.*, 1901, **79**, 792). Large differences in the soluble lead-content of commercial chrome paints were found.

Of 324 samples of crayons submitted, 112 contained lead compounds, and 6 of these also contained arsenic. The lead ranged from 0·7 per cent. to 31 per cent., and the arsenic from 0·2 per cent. to 1·7 per cent. The sample containing the highest proportion of arsenic was coloured with London Purple, a by-product in the manufacture of dyes. London Purple contains a high proportion of calcium arsenite and is used as an insecticide. Thirty per cent. of the lead contained in some of the "chalk" crayons was soluble in the solvent prescribed for the determination of soluble lead in paint.

Only 3 of 38 samples of toys examined were free from lead. Four toy motor cars and one bugle were made of an alloy containing 86 per cent. of lead and 14 per cent. of antimony.

BLACK LIVER IN SHEEP.—Sheep livers and kidneys were examined for the purpose of determining the cause of black liver in sheep. The black livers, which were uniformly black and unsaleable as human food, represented only a very small proportion of the total livers. The health of sheep does not appear to be affected in any way through black liver. The following table gives

	Parts per million (on wet substance)			
Colour of liver	Copper	Iron	Calcium	Sulphur
Black	152	117	162	3,000
Black	263	77	117	2,900
Black	154	90	57	2,884
Black	152	121	75	—
Black (mottled) ..	125	156	920	—
Normal	24	46	81	2,500
Normal	10	76	93	2,800
Normal	4	176	156	—
Normal	42	150	106	—

Although the black livers contained more copper than normal livers, it has not been demonstrated that the blackening is due to the higher copper-content.

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* See also Statutory Rules and Orders, 1926, No. 1621.

International Commission for Uniform Methods of Sugar Analysis*

REPORT OF THE PROCEEDINGS OF THE NINTH SESSION, 1936

THE Ninth Session of the Commission was held at the Institute of Chemistry, London, from August 31st to September 3rd, 1936, when eighty members attended, representing 20 nations. The President was Mr. Frederick Bates, U.S.A., and the Secretary was Mr. Lewis Eynon.

The constitution and by-laws of the Commission were discussed and adopted, and reports and recommendations on the following subjects were presented by the respective Referees, and adopted in each instance.

WEIGHING, TARING, SAMPLING AND CLASSIFICATION OF SUGARS.—It was recommended that uniform international methods of sampling should be elaborated, and that these methods should be based on the experience gained in Czechoslovakia, Germany, Great Britain, Java, Poland and the United States. The method of sampling must depend upon the conditions. The recommendation was made that the various sampling procedures now used in different countries should be made the subject of further study and report.

CONDUCTOMETRIC DETERMINATION OF THE ASH-CONTENT.—The conductometric method was prescribed in Czechoslovakia two years ago and has recently been introduced into Germany. In a study of a large number of determinations it was found that with raw beet sugars the agreement between the results obtained by the chemical and conductometric methods was very close (within 3 per cent. of the amount of ash), but with raw cane sugars the differences were much greater. Such differences are of importance only so long as the gravimetric method is prescribed as the standard method in the valuation of raw sugar. Apart from this, there is no reason for hesitating to introduce the electrometric method, which has the further advantage of giving only the percentage of soluble ash.

DETERMINATION OF REDUCING SUGARS AND THE INFLUENCE OF OVER-HEATING ON THE DETERMINATION OF INVERT SUGAR.—*Determination of Invert Sugar in Refined Sugars, Factory White Sugars, Raw Beet Sugars, Beet Molasses, and Cane Sugars of Low Invert Sugar-content.*—The type of method most likely to command general confidence as an international standard in place of Herzfeld's (which is not sufficiently accurate) is one in which Fehling's solution is replaced by a copper reagent of low alkalinity, containing sodium carbonate instead of hydroxide, and having only a very slight action on sucrose. The Referee (Mr. J. H. Lane) recommended that points of difference in Ofner's method (official in Czechoslovakia), the Luff–Schoorl method (official in Java), and a method worked out at the Berlin Sugar Institute, should be studied and their best features embodied in an International Standard Method for the Determination of Small Quantities of Invert Sugar in Sugar Products.

Determination of Invert Sugar in Raw Cane Sugars.—Recent studies have confirmed the accuracy of the Herzfeld method for cane sugars and indicated that the Munson and Walker method is less accurate. The Luff–Schoorl and Lane–Eynon methods are the most suitable for general use, the former avoiding large sucrose corrections, and the latter being rapid and simple in technique. The Referee recommended that the subject of defecation of cane sugars for invert sugar determinations should be studied.

Determination of Invert Sugar in Cane Molasses.—The Referee recommended that comparative determinations should be made by the Munson and Walker, Lane–Eynon and Schoorl (Java) methods and by the Brown, Morris and Millar method, with particular regard to the concordance obtainable by different chemists with the same method.

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* Printed in England and published by the International Commission for Uniform Methods of Sugar Analysis. Chairman, Publication Committee: Lewis Eynon, 7 & 8, Idol Lane, London, E.C.3. 1937. Price 2s. Issued as a Supplement to *The International Sugar Journal*, January, 1937.

The Report, with a slight amendment, was accepted. Detailed descriptions of some of the newer methods recommended for study are given.

DETERMINATION OF THE DECOLORISING POWER AND FILTERING QUALITY OF CHARS.—The Referee recommended that the quantities of carbons required to give the same decolorising effect as standard carbon (*e.g.* Carboraffin or Norit) should be studied, under standardised conditions (*e.g.* concentration, *p*H, temperature, duration of test, etc.). The relative rate of filtration of the carbon under test should be determined, and a method for determining the revivifying qualities of carbons be defined. The moisture, ash, and effect of the carbon on the *p*H of the solution should be determined; also the apparent sp.gr. and the rate of sedimentation by the method standardised by the Central Laboratory of the Polish Sugar Industry.

TESTING OF MOLASSES.—*Hydrochloric Acid Inversion.*—The Referee presented a critical survey of recent attempts to eliminate various sources of error in the determination of sucrose by acid inversion, and pointed out the desirability of neutralising the acid before the inverted solution is read and adding an equivalent quantity of sodium or potassium chloride to the defecated and de-leaded solution used for the direct reading. He pointed out further the possible effects of the salts present in molasses on the rotation of the sugars and non-sugars. The inversion constant used should be determined on sucrose in presence of the same quantity of salts as in actual analysis.

Invertase Inversion.—The Referee was unable to recommend invertase methods for commercial analysis, since they demand pure yeasts of a suitable culture.

The Report was adopted, together with a recommendation by Mr. C. F. Snyder that "In the analysis of cane and beet molasses the official methods of the National Bureau of Standards be adopted as tentative."

These methods, which are now official in the U.S. Customs Service and in the New York Sugar Trade Laboratory, are given in detail.

APPLICATION OF REFRACTOMETER METHODS TO SUGAR ANALYSIS.—The Referee gave a description of the new dipping refractometers of Zeiss and Askania with the Goldbach flow-through cell attachment, which enables a refractive index to be accurately determined to the fifth place of decimals.

The International Table of Refractive Indices of Sugar Solutions shown opposite was adopted. It is based on the figures of Schönrock–Landt (1933), Schönrock (1911) and Main.

International temperature correction tables for the normal model above and below 20° C. and the tropical model above and below 28° C. were also adopted.

THE 100° S POINT OF THE SACCHARIMETER.—It was suggested that the value 16·269 ± 0·002 g., weighed in air with brass weights, should be adopted as the official normal weight for the French saccharimeter scale. This would bring the International Sugar Scale and the French Sugar Scale into agreement.

STANDARDISATION OF QUARTZ CONTROL PLATES.—Recommendations as to (*a*) optical purity, (*b*) identification marks, and (*c*) plate mountings, were made. It was also suggested that the National Physical Laboratories in Washington, London, Berlin, and Paris should be requested to collaborate and determine: (i) the rotation, in circular degrees, of the 100° S plate for the wave-length (optical centre of gravity) obtained with the Osram sodium vapour arc lamp, (ii) the rotation in circular degrees produced by the Osram sodium vapour arc lamp for plates approximately 25, 50, 75 and 100 S.

EVALUATION OF REFINING QUALITIES OF RAW BEET AND CANE SUGAR.—For raw beet sugars the German type-system, based on colour after a standard affination test, gives a useful measure of affinability, but fuller information as to the best conditions of affination can be obtained by the conductometric affination test. For raw cane sugars the methods of Harman and Honig were recommended.

International Scale (1936) of Refractive Indices of Sucrose Solutions

Per cent.* Sucrose	n_D^{20}	Per cent.* Sucrose	n_D^{20}	Per cent.* Sucrose	n_D^{20}	Per cent.* Sucrose	n_D^{20}
0	1·33299	22	1·36719	44	1·4076	65	1·4532
1	1·33443	23	1·36888	45	1·4096	66	1·4555
2	1·33588	24	1·37059	46	1·4117	67	1·4579
3	1·33733	25	1·3723	47	1·4137	68	1·4603
4	1·33880	26	1·3740	48	1·4158	69	1·4627
5	1·34027	27	1·3758	49	1·4179	70	1·4651
6	1·34176	28	1·3775	50	1·4200	71	1·4676
7	1·34326	29	1·3793	51	1·4221	72	1·4700
8	1·34477	30	1·3811	52	1·4242	73	1·4725
9	1·34629	31	1·3829	53	1·4264	74	1·4749
10	1·34783	32	1·3847	54	1·4285	75	1·4774
11	1·34937	33	1·3865	55	1·4307	76	1·4799
12	1·35093	34	1·3883	56	1·4329	77	1·4825
13	1·35250	35	1·3902	57	1·4351	78	1·4850
14	1·35408	36	1·3920	58	1·4373	79	1·4876
15	1·35567	37	1·3939	59	1·4396	80	1·4901
16	1·35728	38	1·3958	60	1·4418	81	1·4927
17	1·35890	39	1·3978	61	1·4441	82	1·4954
18	1·36053	40	1·3997	62	1·4464	83	1·4980
19	1·36218	41	1·4016	63	1·4486	84	1·5007
20	1·36384	42	1·4036	64	1·4509	85	1·5033
21	1·36551	43	1·4056				

* Grams per 100 grams.

Elimination of Errors due to Lead Clarification in Polarising Raw Sugars.—In view of the fact that the composition and physical properties of basic lead acetate preparations have an important influence on the results, the Referee recommended that the Commission should be authorised to devise suitable tests.

The relative merits of basic lead acetate in solution and in the dry state were discussed, and the following recommendation was adopted: "If no change in the sugar scale is or has been made, clarification shall be effected with standard lead subacetate solution (Third Session of International Commission, Paris, 1900); but if a change from the Herzfeld-Schrönrock scale to the International Sugar Scale is made, then clarification shall be effected with standard dry lead subacetate (Horne's Dry Lead, U.S. Trade Mark)."

Determination of Raffinose.—It was agreed that, in the present state of knowledge, the only methods that could be recommended on theoretical grounds were those depending on the use of enzymes. Any new method for the determination of raffinose must be judged by its capacity to give results in close agreement with those obtained with the basic methods, working with enzymes.

Colorimetry in the Sugar Industry.—The Report recommended that spectrophotometry should be considered the basis of all colour measurements in the sugar industry, the measurements to be made with the monochromatic light of the mercury arc at 435·8, 546·1 and 578·9$m\mu$. It was recommended that an average absolute value suitable for the international definition of a Stammer degree should be published shortly. It is also intended eventually to standardise the preparation of sugar solutions for colorimetry.

CLERGET DIVISORS FOR THE MORE WIDELY USED INVERSION METHODS.—The three branches of the subject—*viz.* (i) Re-determination of Clerget divisor; (ii) specific effect of salts on the Clerget divisor; and (iii) re-determination of the temperature coefficient of the Clerget divisor—are to be submitted to further study.

DETERMINATION OF WATER IN SUGARS AND SUGAR PRODUCTS BY DRYING METHODS.—The following recommendations were accepted by the Commission:

(i) That the standard method for estimation of water in beet molasses, low ash cane syrup, golden syrups, should be carried out in vacuum ovens bled with dry air at 70° C., or preferably 60° C., with a pressure not exceeding 5 cm. Metal dishes with close fitting lids with knob should be used, and for 1 g. of solids approximately, 25 to 30 g. of 40–60 mesh white quartz sand, water being added to facilitate admixture with the sand and drying continued until 2 hourly weighings do not differ by 0·5 mg.

(ii) That refractometer solids corrected for invert sugar should be taken as equivalent to this, or made a subject for further study.

(iii) That the determination of water in cane molasses by drying in vacuum oven as in recommendation (i) should be studied further and compared with drying at lower temperatures, which may obviate decomposition loss being included as water.

Further, in order to obtain a more rapid method for cane molasses, a comparison between drying and refractometric methods, the latter corrected for invert sugar, should also be made to ascertain whether a correction based on ash or conductivity can be used to adjust the refractometer results to agree with those by drying.

DETERMINATION OF HYDROGEN ION CONCENTRATION OF SUGAR FACTORY PRODUCTS.—It was agreed to defer this subject until the next Session of the Commission.

ANALYSIS AND EVALUATION OF REFINED SUGARS.—The Referee suggested that, before the next Session of the Commission, a selection should be made of the tests most widely used in the valuation of refined sugar, that these tests should be investigated and recommendations drawn up for carrying them out in a uniform manner.

The next Session of the Commission was fixed for 1940, in Berlin.

U.S.A. Department of Commerce

National Bureau of Standards

INKS FOR RECORDING INSTRUMENTS*

INKS for recording instruments are made by dissolving dyes in a mixture of glycerin and water. They dry chiefly by being absorbed by the paper, and for this reason lines drawn with them have a tendency to "feather," or have irregular edges. The paper and the nature of the dye determine whether or not there will be feathering.

Instruments for making continuous records of temperature, barometric and steam pressures, electric voltage, etc., may have to run for a long time without attention, so that there must be an ample supply of ink of a kind that will not dry on the pen or freeze in winter. For many years the United States Weather Bureau has used recording ink made by dissolving a dye in a mixture of equal

* Research Paper R.P.935. By C. E. Waters. November, 1936.

volumes of glycerin and water, and for use in certain parts of the United States sufficient ethyl alcohol to keep the ink fluid at any winter temperature is added.

In experimental tests it was found that for indoor use a mixture of 1 volume of glycerin or glycol with 3 volumes of water is a much better solvent than a mixture of equal volumes of the two liquids, and that ethylene glycol is not as good as glycerin at either dilution.

To prevent feathering, as far as possible only the direct dyes should be used. The drawback to the use of some of these dyes is the comparative dullness of their hues. To remedy this, the concentrations were varied so as to get a sufficient depth of colour without causing feathering through non-absorption of some of the dye by the paper. Thus, Congo Red and Diamine Sky Blue FF showed feathering at a concentration of 10 g. per litre, but not at concentrations of 5 and 7·5 g. per litre, respectively. Of the black dyes, Erie Black RX00 could be used at concentrations of 12·5 and 15 g. per litre, and Erie Black RW at 11 g. and 12 g. per litre.

Three or four species of moulds were found on the corks and, in one instance, on the surface of inks prepared with glycerin and water after they had been kept for 3 months, but no mould could be detected on the corks that had been in contact with inks made with ethylene glycol.

Sir George Beilby Memorial Awards

The Administrators of the Beilby Memorial Fund, consisting of the Presidents, Treasurers and Secretaries of the Institute of Chemistry, the Society of Chemical Industry and the Institute of Metals respectively, have announced awards of 100 guineas each to Dr. Bernard Scott Evans and Dr. William Harold Juggins Vernon.

Dr. Evans was educated at Faversham Grammar School and gained his first experience in chemistry in the laboratories of Mr. Leo Taylor, O.B.E., and subsequently with the late Mr. Lawrence Briant, with whom he continued working until the War. He also attended King's College, and graduated B.Sc. (Lond.) in 1904. He passed the Examination for the Associateship of the Institute of Chemistry in 1909, and was elected to the Fellowship in 1915.

In September, 1914, he enlisted in the Artists' Rifles, was gazetted to the Queen's Regiment in 1915, and proceeded to France to join the 4th Suffolks in 1916. In the following year he was seriously wounded and was awarded the M.C. Thereafter he was engaged on scientific work in the Chemical Warfare Department of the Ministry of Munitions, and received the decoration of M.B.E. Since 1919 he has been attached to the Research Department at Woolwich, where he now holds the position of a Scientific Officer. He was awarded the degree of Ph.D. (Lond.) in 1924 and D.Sc. in 1933. He has devised numerous analytical methods for the separation and determination of metals, and contributed the chapters dealing with the methods of analysis applicable to lead, bismuth, arsenic, antimony, tin, iron, chromium, and metallic constituents of steel in Mitchell's "Recent Advances in Analytical Chemistry."

Dr. Vernon received his scientific training at Aston Manor Technical School, Birmingham Municipal Technical School, the University of Sheffield and the University of Birmingham. He graduated B.Sc. (Birm.) in the first division in 1919, Ph.D. (Lond.) in 1924, and D.Sc. (Lond.) in 1927. During the War he served as a leading mechanic and petty officer (R.N.A.S.) at the Royal Naval Experimental Station, Stratford, and was subsequently engaged as Analyst in the Admiralty Laboratories in Birmingham, before resuming his academic post.

In February, 1921, he was appointed Investigator to the newly-formed Atmospheric Corrosion Committee of the British Non-ferrous Metals Research Association. This work, which in 1927 was taken over by the Department of Scientific and Industrial Research, included early quantitative determinations of invisible oxide films on metals, and established a number of generalisations on atmospheric corrosion phenomena (ferrous and non-ferrous).

Dr. Vernon was elected to the Associateship of the Institute of Chemistry in 1920, and to the Fellowship in 1927, in which year he received the Diploma of the Imperial College. His publications have included "A Bibliography of Metallic Corrosion" (Arnold), the First and Second Reports to the Atmospheric Corrosion Research Committee (each of which formed the subject of a General Discussion by the Faraday Society), and other papers in various Transactions or Journals.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Pectin in Milk Products. E. Letzig. (*Z. Unters. Lebensm.*, 1936, **72**, 312–319.)—The use of pectin in food products, especially in milk products, egg-confectionery, sweets, ice-cream and non-alcoholic drinks and also in soap, is likely to increase (Ziegelmayer, *Nahrungsmittelrundschau*, 1935, No. 9). Since it appears that its main use will be in milk products, the author has investigated the problem of its detection in milk, cream, curd and cheese. Pectin was added to these foods in the form of a commercial product, "Lattopekt," available in solid and liquid form. A preparation known as "acid Lattopekt" contains also an organic acid. Liquid Lattopekt contains about 5 per cent. of pectin. In dairy practice, chiefly in the manufacture of edible curds and cheese, the amount of the liquid preparation used varies from 0·25 to 0·5 per cent. of the food. The method for the determination of pectin depending upon its conversion into calcium pectate is not applicable to milk products, owing to the difficulty of obtaining a serum entirely free from albumin. Detection of pectin by liberation of methyl alcohol, for which delicate tests are available, has the disadvantage that large amounts of the sample are required. The method which the author has previously applied to the detection of other thickening agents (*Z. Unters. Lebensm.*, 1934, **68**, 301) has been successfully applied to the detection of pectin in milk products. For the experiments, amounts of Lattopekt varying from 0·25 to 8 per cent. were added to the foods. The serum prepared by acidification with acetic acid was freed from coagulable albumin by boiling and filtering, and its viscosity was determined in Ostwald's viscometer, the relative viscosity being expressed as the time of efflux of the serum, divided by the time of efflux of the same volume of water under the same conditions, the determinations being made at 20° C. The relative viscosity of pure milk serum is about 1·15 and varies only within narrow limits. On the addition of 0·25 per cent. of neutral Lattopekt the viscosity is raised to 1·18, and further additions give correspondingly higher values. The neutral and acid forms of the pectin preparation cause almost identical changes in the viscosity. To determine whether pectin was adsorbed by the precipitated curd the same additions were made to the serum of untreated milk, and it was found that loss of pectin by adsorption is negligible. The following are examples of the figures obtained:

Neutral liquid Lattopekt, per cent.	0·25	0·5	0·75	1·0	2·0	4·0	6·0	8·0
Relative viscosity	1·19	1·23	1·27	1·32	1·49	1·92	2·60	3·29

Cream, after the addition of pectin, gives practically the same results as milk. Curd products are treated as follows:—By simple expression of about 100 g. of curd, 25 ml. of serum are obtained. This is acidified with a single drop of acetic acid, boiled and filtered, and the viscosity of the filtrate is determined. In experiments to determine the normal value for curd serum, it was found that the viscosity of the serum of freshly-prepared curd is approximately the same as that of milk, but that the viscosity increases as the curd ages, presumably because of changes which take place and increase the solubility of the albumin. During ten days' storage of a sample of curd the viscosity of the serum increased from 1·18 to 1·77. To remove this difficulty the viscosity of the curd serum was determined, after which the serum was subjected to the action of a pectin-splitting enzyme (pectolase) for one hour at 37° C., and, after the excess of enzyme preparation had been removed by filtration, the viscosity was again determined. The diminution in viscosity corresponds with the amount of pectin present. The enzyme was added in the form of a commercial preparation, "Bayer N" or "Filtragol." The enzyme had no effect upon the other constituents of the serum. The process was then applied to the examination of cheese. In order to avoid complications due to the presence of micro-organisms and moulds, the cheese to be examined was carefully freed from rind, and only the inner portion was used. Two large samples of cheese were prepared, one containing, and the other free from, pectin. These were stored under conditions favourable to normal ripening, and samples were taken from time to time. During the early stages of ripening sufficient serum could be obtained by simple expression, but in the later stages this became more difficult, and the serum was then obtained in the following manner:—The water-content of the cheese was determined and, after the cheese had been finely shredded, it was allowed to stand for a short time with an amount of water equal to its water-content. The serum was then pressed out, and the amount of added water was removed by evaporation. The viscosity of the serum was determined before and after action of the enzyme. Although, in every instance, the presence of pectin was indicated by a decrease in viscosity after treatment with enzyme, yet, in three weeks, the viscosity of the serum of the treated cheese, after enzymic action, was lower than that of the corresponding portion of the pectin-free cheese. Apparently a slight decomposition of pectin takes place during ripening. The viscosity of the serum of the freshly-prepared pectin-cheese was 1·13, and in three weeks the value had risen through intermediate values to 2·58. These values were unchanged by enzymic action. The cheese containing 0·5 per cent. of liquid Lattopekt gave serum of viscosity 1·21 when freshly prepared, and this value was reduced to 1·13 by enzymic action. The values in three days, one week, and three weeks (the corresponding reduced values after treatment with enzyme being given in brackets) were respectively 1·74 (1·67), 1·74 (1·67), 2·43 (2·38). Provided that the enzyme preparation does not affect other substances which may be present, this method should prove of value for the detection of pectin in other food material.

A. O. J.

Discoloration and Corrosion in Canned Cream. C. J. Jackson, G. R. Howat and T. P. Hoar. (*Tech. Pub. International Tin Research and Dev. Council*, Series A, No. 49, 1937.)—Bronzing, purpling or blackening of tin cans containing cream has been found to be due to tin sulphides produced by the breakdown of proteins when the temperature or the duration of the sterilising process is excessive. The presence of a small amount of sodium bicarbonate, as commonly used as a stabiliser, is probably beneficial in preventing purpling of the can in storage. The existence of exposed steel on the internal surface of the can is detrimental and tends to give rise to black specks of ferrous sulphide in the cream; it is desirable, therefore, that the coating should be as free as possible from pores. S. G. C.

Effect of Time on the Iodimetric Method of Sugar Analysis. H. S. Miller. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1937, **9**, 37–38.)—When glucose and lactose were oxidised, under the same conditions, by an alkaline solution of iodine, the rate of oxidation was lower for lactose than for glucose. The reagents were as follows:—(A) Iodine in potassium iodide solution: 12·69 g. of iodine and 16·60 g. of potassium iodide were dissolved in distilled water and diluted to a litre. (B) Sodium thiosulphate solution: 24·8 g. of the salt were dissolved, and the solution was boiled, cooled and diluted to 2 litres. (C) Sodium hydroxide solution: $N/10$, free from sodium carbonate. (D) Starch solution: Prepared fresh daily. *Method.*—This was essentially that of Kline and Acree (*Ind. Eng. Chem.*, *Anal. Edn.*, 1930, **2**, 413; Abst., ANALYST, 1931, **56**, 48). To 25 ml. of sugar solution in a flask with a ground-in stopper, the iodine and sodium hydroxide solutions are added alternatively in 4-ml. and 7-ml. portions respectively, with shaking after each addition. The temperature is kept at 25° C., and the time is measured from the addition of the iodine and alkali to the sugar solution to the stage at which the solution is acidified slightly with sulphuric acid. The excess of iodine is titrated immediately afterwards with (B). When 100 mg. of the sugar, 35 ml. of (C), and 20 ml. of (A) were used, the optimum time for the oxidation of glucose was 8 minutes; beyond this, over-oxidation occurred. With 100 mg. of lactose monohydrate, only 92 per cent. was oxidised in 8 minutes, but when the amount of iodine solution was increased to 25 ml., optimum oxidation occurred in 15 minutes. A mixture of equal weights of these sugars (50 mg. of each) was more difficult to oxidise than 100 mg. of either, but when 100 mg. of sucrose were added to this mixture, oxidation was complete in 5 minutes and over-oxidation occurred in 15 minutes. The sugars used were glucose, $[\alpha]_D^{25°}$ 52·45 and lactose monohydrate, $[\alpha]_D^{25°}$ 52·90. Optical measurements showed 99·68 per cent. to be the sucrose-content of the sample used. E. B. D.

Development of Acidity in Palm Oil. R. Wilbaux. (*Bull. Matières gras.*, 1936, **20**, 255–257.)—The existence of a lipase in the pericarp of the fruit of *Elaeis guineensis* is confirmed, and its action may be considerably augmented by the presence of mould fungi, particularly of *Mucor* sp., which develop on the site of wounds and at the point of insertion of the drupe stalk. *Aspergillus glaucus* and an oospore type of *Hyphomycetes* have also been found. The lipase action is closely related to the cytoplasmic content and to the presence of calcium ions. Hydrogen ions are deterrent. The action of the lipase diminishes with the increase of free fatty acids, ceasing theoretically when the titre is 45 per cent. The development of rancidity in the fresh oil is not due to the presence of an oxidase in the pulp, nor to enzymes secreted by moulds, etc. Carotene may act as an oxidising catalyst, but the increase in aldehyde in the oil during commercial extraction is small. Storage of the fresh oil in glass vessels causes an increase in acidity of about 0·5 per cent. in 55 days, but this is less if brown glass is used, and less still in iron tanks. Centrifugal treatment of the oil makes it a less favourable medium for mould growth. The fruit should be brought to a temperature of 55° C. as quickly as possible so as to kill the lipase rapidly, and sterilisation of the whole charge will give the best oil, but as this involves conveyance of an extra 50 to 60 per cent. of inert material to the factory the cost of transport and of manual labour may render it impossible. Where manual cleaning is used, certain precautions may be taken to prevent infection by moulds, etc., such as spreading instead of heaping the fruits, cementing of walls and floors, and periodical cleaning with antiseptic solution. D. G. H.

Rancidity in Fats. I. The Effect of Low Temperatures, Sodium Chloride, and Fish Muscle on the Oxidation of Herring Oil. A. Banks. (*J. Soc. Chem. Ind.*, 1937, **56**, 13–15T.)—The catalytic effect of salt on the development of rancidity in bacon fat during storage (Lea, ANALYST, 1931, **56**, 759) is difficult to explain from known data, and the present investigation seeks to elucidate it. The herring oil used was extracted with petroleum spirit from summer herring caught off Fraserburgh, and the course of oxidation was followed by determining the peroxide-content of the fat by a modification of Lea's method. At −5° C. the formation of peroxides reached a maximum in about 45 days, at −10° C. in 110 days, and at lower temperatures it was doubtful if the maximum was reached in 200 days. To find the effect of sodium chloride on oxidation, a volume of lime water requiring 0·55 g. of palmitic acid to neutralise it was made up to 50 ml. with water containing 2·5 g. of salt, and shaken with 50 g. of herring oil containing 0·6 g. of palmitic acid, in an Erlenmeyer flask in which the air had been replaced by nitrogen. Exactly 10 g. of the emulsion were then placed in each of a series of Petri dishes and left at −5° C., together with controls without salt. At intervals dishes were removed, and, after the emulsion had been desiccated with anhydrous sodium sulphate (alkali-free), the oil was extracted with petroleum spirit and the solvent was distilled off, the last traces being removed in a stream of nitrogen under slightly reduced pressure. It was found that sodium chloride had no effect on the rate of atmospheric oxidation of herring oil. Herring muscle (30 g.), water (20 g.), and herring oil (50 g.) were mixed and then emulsified, in some instances with addition of 0·3 g. of sodium chloride, and it was found that the progress of oxidation was of the normal type, but more pronounced in the presence of herring tissue, and still more pronounced when salt was present. The catalytic effect of the muscle was destroyed by heat. It is suggested that an oxidative enzyme system is present in herring muscle. D. G. H.

Studies on the Nature of Antioxygens Present in Natural Fats. III. Occurrence of Antioxygenic Compounds in Extracted Soya-bean Oil cake. T. G. Green and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1937, **56**, 23–26T; *cf.* ANALYST, 1932, **57**, 320, etc.)—The residual material of seeds after extraction of the fatty oil contains considerably higher proportions of oxidation-retarding compounds than the oil itself, but the material requires special treatment before these compounds can be extracted. The preparation of an active anti-oxygenic concentrate from soya-bean cake is described. The extracted meal, after digestion with dilute solutions of organic acids, such as 2 per cent. acetic acid in water or acetone, yields about 10 per cent. of material when heated with methyl alcohol. The part of this extract soluble in cold acetone (about 2 per cent. of the meal) is a viscous gum which, in 0·2 per cent. concentration in distilled unsaturated fatty esters, exerts a marked retarding action on the oxidation of the esters by air at 97·5° C. This concentrate is similar in physical and chemical properties to Olcott and Mattill's material obtained from the unsaponifiable fractions of wheat-germ, cotton-seed or palm oils (*J. Amer. Chem. Soc.*, 1936, **58**, 1627), and also to Dean's concentrate from linseed "foots." The yield of concentrate from the extracted cake is many times greater than from the fatty oils, and the anti-oxygenic compound removed from the seeds with the oil seems to be 2 or 3 per cent. of the total present in the cake, which, however, cannot be removed without a gentle acid treatment followed by an alcoholic solvent. Cellulose has been found not to be the original source of the anti-oxygenic compounds, and organic phosphorus compounds are not regarded as a likely source. D. G. H.

Optical Rotation and Refractivity of Nicotine and Nicotine Sulphate in Dilute Aqueous Solution. F. G. H. Tate and L. A. Warren. (*J. Soc. Chem. Ind.*, 1937, **56**, 39–40T.)—The pure nicotine used for the determinations was prepared from the crude material by Lowry's modification of Ratz' method (*J. Chem. Soc.*, 1929, 1376), and had the following constants:—d^{20}_{4}, 1·0096; $[\alpha]^{20}_{D}$, $-169{\cdot}4°$; $[\alpha]^{20}_{546{\cdot}1}$, $-204{\cdot}2°$. The specific rotation, the rotation of mean yellow light measured in sugar (Ventzke) degrees, and the refraction by the Zeiss immersion refractometer were determined for aqueous solutions of nicotine and nicotine sulphate at concentrations of 0 to 10 per cent. The values of the specific rotations were constant for each substance: for nicotine $[\alpha]^{20}_{D}$, $-79{\cdot}4°$; $[\alpha]^{20}_{546{\cdot}1}$, $-96{\cdot}1°$; and for nicotine sulphate $[\alpha]^{20}_{D}$, $+14{\cdot}3°$; $[\alpha]^{20}_{546{\cdot}1}$, $+17{\cdot}2°$. The Zeiss readings for both nicotine and nicotine sulphate solutions increased proportionately with the concentrations from 0 to 10 per cent.: 5·41 units per 1 per cent. increase in concentration for nicotine, and 5·13 units for nicotine sulphate. D. G. H.

Alkaloids of the Genus *Senecio*. J. J. Blackie. (*Pharm. J.*, 1937, **138**, 102–104.)—This genus of plants, which is used medicinally, contains appreciable amounts of well-defined alkaloids. British species are considered harmless, but those of Canada, New Zealand, South Africa, and Norway have caused diseases in cattle, and in South Africa cases of illness and death have been traced to flour ground from wheat containing seeds of *Senecio ilicifolius* and *S. burchelli*. The symptoms were gastric disturbance with enlargement of the liver. There are two groups of *Senecio* alkaloids: I. Alkaloids very soluble in chloroform and containing 18 carbon atoms. II. Alkaloids partly soluble in water, very soluble in chloroform, and containing 12 carbon atoms. In this investigation three South African and twelve British species have been examined. The South African species contained alkaloids of Group I. Alkaloids of this group were also found in nine of the British species, and those of Group II in three British species. The alkaloid-content of the South African species was much higher than that of the British ones. *S. isatideus* (poisonous ragwort or Dan's cabbage), which is widespread in South Africa, contained 1·14 per cent. of isatidine, a new alkaloid, and 0·15 per cent. of retrorsine. Retrorsine was also present in the other South African species. *S. glaberrimus* contained 0·027 per cent., and *S. venosus* 0·01 per cent., of retrorsine. The results for British species were as follows:

Species	Alkaloids Per Cent.	Date
Senecio vulgaris (groundsel) ..	0·015	April
	0·06	June
	0·015	September
S. squalidus	0·06	July, 1935
S. viscosus	0·06	July, 1934
	0·28	Early summer
S. Jacobaea (common ragwort)	0·03	June, 1934
	0·057	July, 1934
S. aquaticus (marsh ragwort) ..	0·04	July
	0·018	September
S. cineraria	0·052	
S. erucifolius	Trace	
*S. paludosus**	0·0015	
*S. palustris**	0·001	

* These species, being rare in this country, were obtained from Holland.

The alkaloid of the April and September groundsel was pure senecionine; this was also present, together with another alkaloid, in the June sample. It occurred pure in *S. viscosus* and, mixed with a little squalidine (a new alkaloid), in *S. squalidus*. Alkaloids of the other species were difficult to obtain pure and are still being investigated. Group II.—Alkaloids of this group were present in *S. sylvaticus*, *S. saracenicus*, and *S. campestris*, var. *maritimus*. They were obtained as syrups, and were usually purified by fractional crystallisation in a high vacuum.

Method of analysis.—The coarsely powdered dried substance was extracted repeatedly with alcohol until the alcoholic extract gave no reaction with Mayer's reagent. The alcohol was distilled off *in vacuo*, and the extract, which contained much chlorophyll and resinous matter, was then treated with 2 per cent. hydrochloric acid and filtered, and the colouring matter was removed from the filtrate by extraction with ether. The filtrate was made alkaline with ammonia, and the alkaloids were extracted by shaking with successive quantities of chloroform. By repeating the treatment with acid and chloroform the alkaloids were obtained in crystalline condition. Group II.—The general process of extraction was as described above, but, as the alkaloids were obtained as syrups, further treatment was necessary. Details of the methods of separation, purification and identification of the individual alkaloids in the various species examined are given for both groups, and the constitutions of those of Group I are discussed. All alkaloids of this group yield the basic fission product retronecine, $C_8H_{15}O_2N$, which on reduction yields retronecane, $C_8H_{15}N$, which is isomeric with the tropane of solanaceous alkaloids and with heliotrin, an alkaloid of *Heliotropium lassocarpum*. All the *Senecio* alkaloids appear to have a heterocyclic five-membered ring which gives the pyrrole reaction by distillation with zinc dust. Senecionine and squalidine were described by Barger and Blackie (*J. Chem. Soc.*, 1936, 743). E. B. D.

Determination of Lipase in Official Preparations of Pancreatin. H. Penau and J. Guilbert. (*J. Pharm. Chim.*, 1937, **25**, 5–17.)—The method recommended is as follows:—A 1 per cent. solution of agar-agar is made up by swelling 10 g. of agar-agar, cut into small pieces, in about 200 ml. of water for 4 hours, straining through gauze, and dissolving the agar-agar in 800 ml. of boiling water, with constant stirring. The *p*H is adjusted to 7 by adding a few drops of dilute sodium hydroxide solution, the weight is made up to 1000 g., and the liquid is heated in an autoclave at 120° C. for 15 minutes, and filtered through a hot funnel. Twenty-ml. portions are sterilised in test-tubes, closed with sterilised cotton, for 20 minutes at 115° C., and covered with sterilised rubber caps to prevent evaporation. Into a 60-ml. flask with ground glass stopper are put, in the order given, 0·6 g. of glycine, 2 ml. of *N* sodium hydroxide solution, and 8 ml. of distilled water warmed to 40° C., followed by 40 mg. of a mixture of pancreatin and lactose (1 per cent. of pancreatin). The mixture is carefully shaken and treated with 10 ml. of the 1 per cent. agar-agar solution (warmed to 40° C.), and 1·5 ml. of purified tributyrin. After shaking, the liquid is kept in a water-bath at 40° C. for 2 hours; during the first half-hour the flask is shaken for 30 seconds every 5 minutes, and then for 30 seconds every 10 minutes. The *p*H must still be greater than 8·4 (pink with phenolphthalein). The action of the enzyme is stopped by the addition of 1 ml. of a 10 per cent. solution of sodium metaphosphate and 5 ml. of *N* sulphuric acid. The flask is shaken and cooled in a refrigerator. Extraction with ether is carried out at once or within 3 hours after this. The contents of the flask are transferred to a 300-ml. separating funnel, and the flask is washed out twice with 3 ml. of distilled water, first the stopper and then the neck being washed each time. The aqueous solution is extracted four times with ether, 50 ml. being used for the first and 25 ml. for the later extractions. The ethereal extracts are combined and washed, first with 2 ml. and then with 1 ml. of distilled water, and transferred to a 500-ml. conical flask. Fifty ml. of absolute alcohol and 10 ml. of water are added, and the liquid is titrated with *N*/10 sodium hydroxide solution to the end-point of bromophenol blue (1 ml. of a 0·04 per cent. solution). A blank test is made on an aqueous solution previously boiled for 2 minutes. It is suggested that for a pancreatin of Codex quality the difference between the two titration values should not be less than 10 ml. of *N*/10 sodium hydroxide solution. E. M. P.

Distinguishing Reactions of the Principal Silver Colloids. R. Deschaseaux. (*J. Pharm. Chim.*, 1937, **25**, 29–30.)—Vaille (*J. Pharm. Chim.*, 1934, **19**, 256; Abst., ANALYST, 1934, **59**, 422) has proposed reactions for distinguishing between argyrol, collargol, electrargol, and protargol. In the present paper, tests are described for discriminating between 1 per cent. pseudo-solutions of collargol, argyrol, vitargyl, silver vitellinate, and silver proteinate. One ml. of the pseudo-solution is treated with 1 ml. of a solution containing crystallised sodium thiosulphate 10 g., dry sodium chloride 1 g., and distilled water to 100 ml. Collargol, argyrol, and vitargyl give precipitates with this reagent. After 30 minutes the flocculate is filtered off. For the second test the biuret reaction is applied to the filtrate from the first. The liquid containing collargol is the only one that does not give the reaction. For distinguishing argyrol from vitargyl, and vitellinate from proteinate, 2 drops of pure crystallisable acetic acid are added to 1 ml. of the pseudo-solution. Vitargyl and vitellinate give immediate precipitates with the acid. E. M. P.

Biochemical

Determination of the Place of Absorption of Halogen Derivatives of Ethylene in the Body. Le Bihan. (*J. Pharm. Chim.*, 1937, 25, 20–23.)—Dogs were given repeated inhalations of the vapour of the solvent under examination, and were finally killed after a large dose. The organs were reduced to pulp and heated in a water-bath in the presence of a dilute solution of tartaric acid, while a current of air is drawn through them by means of the following train of apparatus:—A bubbler containing silver nitrate solution, the flask containing the organ, a second silver nitrate bubbler, all immersed in the water-bath, a quartz tube heated to 1000° C. in an electric furnace, a third silver nitrate bubbler, and a final bubbler to detect any residual hydrogen halide. The silver halide precipitated in the third bubbler was determined, and the quantity of solvent given up by the organ was calculated. The results of one experiment were as follows:

Animal: dog weighing 11 kg., given 7 doses of anaesthetic, the duration of the last dose being 50 minutes.

Organ	Weight of organ taken g.	Tetrachloroethane estimated mg.	Mg. of tetrachloroethane per 100 g. of organ
Bone marrow ..	0·60	0·518	85·92
Suprarenals	1·158	0·814	70·34
Thyroids	0·818	0·408	49·92
Brain	24·8	3·957	15·91
	35·2	6·856	19·4
Kidney	23·62	3·102	13·13
	22·60	2·929	12·97
Blood	30 ml.	3·2	10·66
	24 ml.	2·65	11·04
Liver	56·35	40·15	71·2
	51·6	43·3	83·8
Lungs	20·70	12·85	62·08
Testes	17·42	1·27	7·28
Pancreas	10·26	1·27	12·37
Abdominal fat ..	11·89	10·83	91
Spleen	13·25	0·804	6·07
Muscles	47·23	2·604	5·51
Urine	30 ml.	2·55	8·5

The anaesthetic was absorbed in large quantities by the organs rich in lipoids, the liver, brain, spleen, and lungs, and also by the endocrine organs, the suprarenals, thyroids, and particularly the marrow of the bones. In a further experiment to determine how long the anaesthetic was retained, samples of blood from anaesthetised dogs were removed periodically and examined. The results were as follows:

Dog anaesthetised for 10 *minutes.*

Time	Tetrachloroethane per 100 ml. of blood mg.
During anaesthesia	10
1 hour 50 minutes later	7·33
3 hours 30 minutes later	7·08

Dog anaesthetised for 13 *minutes.*

Time	Tetrachloroethane per 100 ml. of blood mg.
During anaesthesia	12·7
3 hours 45 minutes later	9·95
8 hours later	4·91
27 hours 15 minutes later	0·864

E. M. P.

Determination of Bases from Animal Tissues. E. Strack and H. Schwaneberg. (*Hoppe Seyler's Z. phys. Chem.*, 1936, **245**, 11–18.)—It has been found possible to use ammonium reineckate for the separation of choline from carnitine or betaine and to determine the amount of each present in solution. The chlorides of choline and carnitine are dissolved in about 500 times their weight of water at room temperature, made definitely alkaline to litmus with ammonium hydroxide, and an excess of ammonium reineckate solution is added. The solution must not be more concentrated or carnitine reineckate will be carried down by the choline salt and require a considerable amount of washing for its separation. After standing for about 30 minutes, fine silky crystals of choline reineckate are precipitated. These are filtered off, washed with a little water, dried and weighed. If the filtration is difficult, a little kieselguhr may be added; the choline reineckate is then removed by washing with a mixture of acetone and water, the solution is evaporated, and the residue is weighed. The choline reineckate is decomposed by the addition of silver sulphate and barium chloride, and the choline is assayed biologically as the acetyl derivative. Larger amounts may be identified chemically as the gold salt (long standing in ammoniacal solution and subsequent drying causes decomposition of part of the reineckate so that the acetone-water mixture will not dissolve it completely and the biological assay is low). For the determination of carnitine or betaine the ammoniacal filtrate from the choline precipitation is made acid to Congo red with hydrochloric acid, and more ammonium reineckate is added. The solution is allowed to stand for one hour on ice, after which the crystals are filtered off, with the aid of suction, washed with a little cold acidified water, dried and weighed. After decomposition, a portion may be acetylated and assayed biologically and the rest converted into the gold salt. By this method it is claimed that small amounts of choline in the presence of betaine or carnitine can be separated with a fair degree of accuracy. Betaine reineckate behaves in the same way as the carnitine salt. S. G. S.

Studies on Ketosis. Quantitative Studies on the Oxidation of the Ethyl Esters of the Fatty Acids. H. J. Deuel, L. F. Hallman, J. S. Butts and S. Murray. (*J. Biol. Chem.*, **1936**, **116**, 621–639.)—The administration of ethyl acetoacetate, ethyl butyrate or ethyl caproate to fasting rats resulted in a uniform ketonuria which was somewhat lower than that produced by the sodium salts of the acids. More than twice the degree of ketonuria was observed after the ingestion of the ethyl esters of caprylic, capric, lauric and myristic acids than was found in the acetoacetate controls. This was held to indicate that two fragments capable of forming acetone bodies are produced per molecule of fatty acids. When ethyl palmitate or ethyl stearate was administered in oil in one-eighth the dose employed in the above tests, or ethyl oleate without oil in a somewhat larger dose, the excretion of acetone bodies was greater than that with the laurate or caprylate controls. This suggests that the molecule of palmitic, stearic or oleic acid breaks up into at least three fragments, which are capable of being converted into acetone bodies. No appreciable ketonuria followed the administration of the ethyl esters of propionic, valeric, heptoic, pelargonic or undecylic acid. It is suggested that caproic and butyric acids, as well as the odd-chain carbon acids, break down chiefly by β-oxidation. The even-chain carbon acids containing 8 to 14 carbon atoms are probably also broken down by δ- and ζ-oxidation by "multiple alternate oxidation," as suggested by Jowett and Quastel. Since ethyl caprate is as good a ketogenic agent as ethyl caprylate, it is possible that its chief mode of oxidation is to acetone bodies rather than to dicarboxylic acids as suggested by Verkade and van der Lee. Acetone is the only important β-ketone excreted in the urine after the administration of the higher even-chain fatty acids. S. G. S.

Fluoresceinuria. G. Discombe. (*Lancet*, 1937, **232**, 86.)—If a urine is normal in colour but has an intense grass-green fluorescence, the presence of fluorescein should be suspected. If it is present, an absorption band between 506 and 482$m\mu$ (maximum at 494$m\mu$), *i.e.* almost identical with that of urobilin, with general absorption on the blue side of 430$m\mu$, can be observed. Both the fluorescence and absorption band disappear if the urine is acidified with hydrochloric acid. Ephazone, a proprietary remedy for asthma, produces these effects, most of the dye being excreted during the 4 hours after administration, although excretion is still incomplete after 8 hours. The dye is separated by acidifying 50 to 500 ml. of urine with 1 to 2 ml. of conc. hydrochloric acid and extracting with 25 ml. of amyl alcohol. The extract is then itself extracted, first with 100 ml. of water containing 20 drops of a 40 per cent. sodium hydroxide solution, and then with 50 ml. of water, 50 ml. of (presumably ethyl) alcohol being added to the combined washings, which are then diluted to 250 ml. The solution should be clear, and if 1 part of dye was present in 5,000,000 parts of the urine it should show the characteristic fluorescence, absorption and yellow colour. The dye may be identified by converting it into eosin (*cf.* Grant, ANALYST, 1936, **61**, 400), 100 ml.

of the solution acidified with hydrochloric acid being mixed with 1 ml. of bromine water and made alkaline with sodium hydroxide, when the liquid becomes pink and has a yellow-green fluorescence. Fairly concentrated solutions have an absorption band between 515 and 525*mμ* (*b* to *E* lines), but thick layers of liquid should be examined if the solution is dilute, as an excess of bromine may have destroyed some of the eosin. The fluorescence test provides a more sensitive test for both dyes than the absorption band. Solutions of eosin in water (or dilute ethyl alcohol) and in amyl alcohol showed, respectively, one band between 434 and 560*mμ* (maximum at 515 to 525*mμ*), and one or two bands, according to the concentration, at 532*mμ* (intense) and 496*mμ* (weak and diffuse). Eosin in urine may be identified by extracting a mixture of 200 ml. of sample and 1 to 2 ml. of strong hydrochloric acid with 25 ml. of amyl alcohol, and examining the extract after addition of an excess of solid sodium acetate. A 1-inch layer of extract from urine containing 1 part of eosin in 5,000,000 showed the band at 532*mμ*. One hour after the administration of 0·1 g. by the mouth the dye was present in the urine, but it could not be detected after the sixth hour. J. G.

Irradiation of Fats. Some Observations on Methods of Analysis of Oxidised Fats and on the Interrelation of the Results obtained. L. H. Lampitt and N. D. Sylvester. (*Biochem. J.*, 1936, **30**, 2237–2249.)—A method of evaluating the intensity of the Kreis test colour by the use of the Zeiss photometer; an improved method of determining the Issoglio value, incorporating the use of a stream of nitrogen for stirring the fat during the period of aqueous extraction; and a modification of Lea's method for the determination of peroxides are described. For full details of these methods the original paper should be consulted. The peroxide value after the Issoglio determination showed a decrease of 16 per cent. on that obtained before this determination, the Kreis test intensity was reduced by about 55 per cent., and the aldehyde value by about 55 per cent. from the same cause. These figures were independent of the degree of oxidation of the fat. The Issoglio value appeared to be proportional to the reduction in the aldehyde value and also to the aldehyde value of the original fat. The peroxide and aldehyde values were roughly proportional, and therefore the former was also proportional to the Issoglio value. S. G. S.

Isolation of the Antirachitic Vitamin from Halibut-liver Oil. H. Brockmann. (*Hoppe-Seyler's Z. phys. Chem.*, 1936, **245**, 96–102.)—From 150 kg. of halibut livers 300 g. of a concentrate containing 120 international units of vitamin *D* per mg., and 2000 C.L.O. units of vitamin *A* per mg. were prepared by the method described in the German patent, D.R.P. 634,760. When 130 g. of this concentrate were dissolved in benzine and the solution extracted 16 times with 90 per cent. methanol, the benzine solution yielded 58·5 g. of fraction (i) containing 700 C.L.O. units of vitamin *A* per mg., and the methanol extract contained 49·5 g. of fraction (ii) containing 2500 C.L.O. units of vitamin *A* per mg. Fraction (i) was then dissolved in benzine, and the solution was extracted 12 times with 95 per cent. methanol. From the benzine solution 23 g. of fraction (iii), containing 400 C.L.O. units of vitamin *A* per mg., was obtained, and the methanol extract contained 24 g. of fraction (iv) whose vitamin *A* content was 1000 C.L.O. units per mg. Fraction (iv) was dissolved in benzine and extracted with 90 per cent. methanol. From the benzine solution 20 g. of fraction (iv*a*) was obtained. This had a vitamin *A* content of 470 C.L.O. units per mg. and a vitamin *D* content of 600 international units per mg. Fraction (iv*a*) was then subjected to adsorption on aluminium hydroxide III. For this purpose 27 g. were mixed with 200 mg. of Indicator-red 33 and dissolved in a mixture of one part of benzine and four parts of benzene. The same solvent was used for washing the column. Elution of the aluminium hydroxide gave 8·5 g. of an oily substance [fraction (v)], and from the filtrate 16·7 g. of fraction (vi) (also an oil) were obtained. When this process was repeated with 7·5 g. of fraction (vi), four zones were obtained. Zone 2, which consisted of the red colour and the vitamin, contained 2·9 g. of fraction (vii), which had a potency of 2400 international units of vitamin *D* per mg. The other zones were neglected. The process was repeated, using 6 g. of fraction (vii) and the same solvent as before. Three zones were obtained, Zone 1 was neglected, Zone 2 contained 2·85 g. of an oil having a vitamin *D* content of 5000 international units per mg. and Zone 3 contained 0·3 g. of an oil with an activity of 6000 international units per mg. Zone 2 became a fraction (viii) and Zone 3 fraction (ix). From fraction (viii) the sterols were removed, first by freezing and finally by precipitation with digitonin. The difference between these fractions was due to different sterol contents. Both fractions were then esterified with 3:5-dinitrobenzoylchloride in pyridine. The ester from fraction (viii) was again subjected to the chromatogram, the zone containing the vitamin was extracted with acetone, and after the addition of methanol the ester was allowed to crystallise. The crystals were extracted with petroleum spirit, in which the vitamin ester was soluble and the residue was found to consist of the esters of the higher alcohols. When the residue from the petroleum spirit solution was recrystallised, a product melting at 126° C. was obtained. After further recrystallisation from diluted acetone the m.p. had risen to 128°–129° C., and showed no depression when mixed with the 3:5-dinitrobenzoate from tunny-liver oil or with that from irradiated 7-dehydrocholesterol. The carbon and hydrogen percentages obtained by analysis agreed with those for the theoretical formula. When fraction (ix) was subjected to the same procedure, similar results were obtained. It is therefore claimed that the antirachitic vitamin isolated from halibut-liver oil is the same as that previously obtained from tunny-liver oil, and that both are identical with vitamin D_3.

S. G. S.

ABSTRACTOR'S NOTE.—In each instance the ester has been isolated and identified. The crystalline vitamin has not yet been obtained.

Influence of Fertilisers on the Carotene and Vitamin *C* Contents of Plants. J. B. H. Ijdo. (*Biochem. J.*, 1936, 30, 2307–2312.)—When spinach was used as the experimental plant it was found that an increase in the nitrogen-content of the soil resulted in an increase in the carotene and vitamin *C* contents of the leaves. When the amount of potassium in the soil was increased, the carotene-content decreased, but the vitamin *C* content was increased. Under the conditions of the experiments the influence of calcium salts, magnesium salts or phosphates was negligible. It is suggested that there is a relationship between vitamin *C* content and photosynthesis on the one hand, and between the chlorophyll-content and carotene on the other hand. It was found that analyses had to be made rapidly, for storage for a few days, even in ice, caused a large reduction in the amount of vitamin *C* found. S. G. S.

Amount of Ascorbic Acid in Blood and Urine. The Daily Human Requirements for Ascorbic Acid. M. van Eekelen. (*Biochem. J.*, **1936, 30, 2291–2298.**)—The ascorbic acid content of the blood, and the amount excreted in the urine, depend upon the quantity ingested and the amount stored by the organism. Saturation of the organism coincides with a certain level in the blood (about 13 mg. per litre). When this level is passed, the surplus amount is excreted in the urine. The determination of the ascorbic acid content of the blood has proved to be the most reliable means of ascertaining the state of saturation of the organism. The daily requirements are dependent on the amount stored by the organism and are largest when the subject does not become markedly unsaturated. The daily dose for adults weighing 70 kg. is about 60 mg. under normal conditions. In all the determinations carried out, interfering substances were removed by precipitation with mercuric acetate in accordance with previously described technique. (See also the following abstract.) S. G. S.

Relation between Diet and Urinary Output of Thiosulphate (and Ascorbic Acid). Human Requirements for Vitamin *C*. M. Heinemann. (*Biochem. J.*, 1936, **30**, 2299–2305.) The urinary output of ascorbic acid, determined after treatment with mercuric acetate, has been found to be independent of the amount of protein in the diet. The total reducing capacity of the urine, however, rises and falls in direct relationship to the quantity of protein in the food and depends chiefly on the output of thiosulphate. The amino-acids containing sulphur are probably the source of the thiosulphate in the urine, for, when cystine is ingested with a low protein diet, the effect on the total reducing capacity of the urine is the same as when the diet contains a large amount of protein. The daily requirement for man was found to be 60 mg. for a body weight of 70 kg. (See previous extract.) The same amount was required when 25 or even 37·5 mg. of "Redoxon" per day had been taken. This is regarded as *the actual requirement*, and from this work and other published results the *indispensable minimum* appears to be about half this amount. S. G. S.

Estimation of Ascorbic Acid as Furfural and a Comparison of Results obtained by this Method and by Indophenol Titration. J. H. Roe. (*J. Biol. Chem.*, **1936, 116, 609–619.**)—The method consists essentially in the estimation of the furfural formed by boiling an acid extract of a tissue, in which the ascorbic acid has been oxidised by shaking in presence of Norit, with hydrochloric acid alone and with hydrochloric acid containing stannous chloride. The difference between these values is the amount of furfural from ascorbic acid. Furfural is determined by the colour formed with aniline, stabilised with stannous chloride and proper amounts of acetic acid. The hydrochloric acid solution of stannous chloride is prepared by adding 5 parts of conc. hydrochloric acid to 1 part of water and dissolving 4 g. of stannous chloride in 40 ml. of this solution. The Norit is prepared by placing 100 g. of Norit in a large flask, adding 1 litre of 10 per cent. hydrochloric acid and heating to boiling, filtering the suspension with the aid of suction, and washing with water until the washings are free from chlorides. The carbon is then heated gently until the water has evaporated and finally to redness for 15 minutes. An alcoholic solution of aniline is prepared by dissolving 1 part of colourless re-distilled aniline in 2 parts of 95 per cent. ethyl alcohol. If ascorbic acid is used as the standard solution, the standards must be freshly prepared each day. It has been found possible to use as a standard a solution of xylose in a saturated aqueous solution of benzoic acid, of such strength that 1 ml. is equivalent to 0·1 mg. of ascorbic acid. This solution must be compared with one of ascorbic acid for furfural formation, but the authors found that, under their conditions, 123 mg. of xylose in 1 litre of saturated benzoic acid solution gave the required values. The ascorbic acid in plant tissues is estimated by grinding 10 g. of the tissue in a mortar with sand under about 50 ml. of a 1 per cent. solution of oxalic acid. A funnel containing a mat of gauze is placed in a 100-ml. volumetric flask and the ground material is poured upon the gauze. The gauze is sqeezed until fairly free of solution and the solid material is returned to the mortar. About 10 ml. of the oxalic acid solution are added, and the mixture is ground again and returned to the gauze filter. The material on the filter is squeezed dry and washed with the oxalic acid solution which has been used previously for washing the sand in the mortar. The washing is continued until the fluid in the flask reaches the 100-ml. mark. The contents of the flask are mixed thoroughly, and 20 ml. of this solution are now placed in a small flask and solid calcium carbonate is added in excess. When the solution has been neutralised (as indicated by Congo red paper), 1 g. of Fleischmann's yeast is added. A pure strain of yeast, free from vitamin "supplements" should be used, or difficulty will be experienced in clarifying with charcoal. The flask is stoppered loosely and placed in an incubating oven at 38° C. until the fermentable sugar has been removed (about 1 hour). The liquid is transferred to a centrifuge tube, and the solids are removed by centrifugation. Ten ml. of the clear liquid are added to 2 ml. of glacial acetic acid in a small flask. About 0·5 g. of the acid-washed Norit are added, and the flask is shaken for 2 minutes, after which the solution is filtered.

For the estimation of total furfural, 1 ml. of the filtrate from the Norit treatment is placed in a test-tube, about 15 × 200 mm. In each of three similar tubes is placed 1 ml. of standard ascorbic acid (xylose) solution, such that the standards are equivalent to 0·1, 0·05 and 0·03 mg. of ascorbic acid per ml. To each tube 1 ml. of the hydrochloric acid solution of stannous chloride is added. The tubes are placed in a boiling water-bath for 15 minutes, after which they are removed and cooled. To each tube 2 ml. of glacial acetic acid are added in such a manner that it flows down the sides of the tubes and removes any condensed water. Three ml. of alcoholic aniline solution are now added to the tubes, so that a layer is formed. Finally the contents of the tubes are thoroughly mixed by shaking and then allowed to stand for 10 minutes to allow the maximum colour development, and the unknown is compared in a colorimeter with the standard which most closely matches it. The non-ascorbic acid furfural is estimated by placing 1 ml. of the Norit filtrate in a test-tube of the size previously described, and adding to each of three similar tubes 1 ml. of the ascorbic acid standards, choosing the equivalents of 0·03, 0·02 and 0·01 mg. of ascorbic acid per ml. To each tube 1 ml. of a 30 per cent. solution of hydrochloric acid is added. The tubes are placed in a boiling water-bath for 15 minutes, after which they are removed and the contents are cooled. To each tube 1 ml. of a freshly prepared 1 per cent. aqueous stannous chloride solution is added, followed by 2 ml. of glacial acetic acid and 3 ml. of alcoholic aniline solution. The contents of the tubes are mixed, and the procedure described above is followed. For vegetable or fruit juices, the juice is diluted to 10 volumes, and, if acid, is treated with excess of solid calcium carbonate. From this point, the procedure is that described for the neutralised oxalic acid extract of tissues. Sometimes 2 hours may be necessary for the completion of the fermentation.

For animal tissues, the material is ground with sand and 6 volumes of a 5 per cent. sulphosalicylic acid solution in 10 per cent. acetic acid. The extract is filtered through gauze, and the residue is washed with similar solution until 10 volumes are obtained. The extract and washings are mixed and centrifuged. To 10 ml. of the clear liquid 0·5 g. of the acid-washed Norit are added, the whole is shaken for 2 minutes and filtered, and from this point the procedure is as described above. Liver tissue is assayed by grinding with the sulphosalicylic-acetic acid mixture followed by the Norit treatment as before. To 5 ml. of the Norit filtrate an equal volume of absolute ethyl alcohol is added to precipitate the glycogen. The solution is mixed and centrifuged. The subsequent procedure is as previously described, except that 2 ml. of the alcoholic filtrate are used and 1 ml. of absolute alcohol is added to each standard tube. Recovery of added ascorbic acid varied from 94 to 100 per cent. This method was compared with the indophenol titration, using Tillman's method but extracting the material with 10 volumes of the sulphosalicylic-acetic acid mixture. Close agreement was obtained between the two methods upon brain, heart, intestine, kidney, spleen, adrenal glands, lens and aqueous tumour of the eye and plant tissues, but with liver the titration method gave results 25 per cent. higher than the colorimetric method. The results indicate that in the plant and animal tissues examined ascorbic acid exists in the reduced form only. S. G. S.

Effect of Light on the Vitamin *C* of Milk. S. K. Kon and M. B. Watson. (*Biochem. J.*, 1936, **30**, 2273–2290.)—Milk which originally gave a positive chemical test for vitamin *C* failed to reduce the indophenol reagent after exposure to daylight through glass. The reducing power was restored to a varying extent by treatment with hydrogen sulphide, but irreversible losses always occurred. Visible light of short wave-length (blue and violet) was chiefly responsible for the reaction, and ultra-violet light was also probably active, but yellow and red light had practically no effect. The presence of oxygen was necessary for the action of light, and the reversible oxidation taking place followed the laws of a unimolecular reaction, having a temperature coefficient of 1·4 for a range of 0° to 37° C. It is probably a chain reaction. The decomposition of the reversibly oxidised ascorbic acid is a more complicated reaction which remains incomplete. It is suggested that the effect of light on the ascorbic acid of milk is a part of the general oxidative changes induced in milk by the actinic activation of oxygen. It is also suggested that the mechanism of the breakdown of the ascorbic acid is similar to the known oxidation decomposition of this substance, namely, that dehydroascorbic acid is formed in the reversible oxidation, and that the opening of the lactone ring takes place in the course of the further irreversible changes. Synthetic ascorbic acid added to milk, behaves, under the action of light, in the same way as the ascorbic acid originally present. Tests on guinea-pigs confirm the chemical findings. A pint bottle of milk exposed to the sun under conditions likely to occur in practice, on the door-step for half-an-hour, and then kept for 1 hour in the dark, lost half of its original antiscorbutic properties. Milk as secreted by the normal cow contains only reduced ascorbic acid, but when this milk is pasteurised by the holder method, any reversibly oxidised ascorbic acid is destroyed, whilst the reduced form is not affected. In the absence of catalytic metals, the amount of vitamin *C* destroyed by pasteurisation depends on the previous exposure of the milk to light. S. G. S.

Vitamin *C* in Vegetables. Ascorbic Acid Oxidase. Z. I. Kertesz, R. B. Dearborn and G. L. Mack. (*J. Biol. Chem.*, 1936, **116**, 717–725.)—Ascorbic acid oxidase, which has been reported in cabbage and squash, has also been found in many other vegetables, but the relative activity of the enzyme varies greatly in different vegetables. The presence of this enzyme, which is completely inactivated in vegetables or their extracts by heating at 100° C. for 1 minute, is instrumental in the loss of physiologically active forms of ascorbic acid by catalysing the formation of dehydroascorbic acid, which is more readily decomposed by a non-enzyme reaction into a compound having no antiscorbutic activity. Peas frozen after sufficient heat-treatment to inactivate the ascorbic acid oxidase retained a much greater portion of their original ascorbic acid content than those having the active enzyme present. Since the ascorbic acid oxidase and catalase appear to be inactivated by heat at the same rate, the commercial practice of establishing the proper blanching time by a test for catalase activity also yields information on the inactivation of the ascorbic acid oxidase. S. G. S.

Bacteriological

Parachlorometaxylenol as a Preservative. E. A. Lam. (*Pharm. J.*, 1937, **138**, 76.)—The chlorinated xylenols are being increasingly used as non-poisonous antiseptics and disinfectants in saponaceous solution, but there does not appear to have been any published information about their use as preservatives for bacterial preparations such as vaccines. Parachlorometaxylenol (1-hydroxy-3 : 5-dimethyl-4-chlorobenzene) is a white crystalline powder with a phenolic odour which in a saponaceous solvent has a Rideal–Walker coefficient of about 60 (*Pharm. J.*, 1936, **197**, 273), and in 3 per cent. saponaceous solution a coefficient of 1·6. Phenol and cresols, which are normally used for the preservation of vaccines, have been criticised because of their inefficiency.

An experiment is recorded on the use of 0·5 per cent. phenol together with 0·035 per cent. parachlormetaxylenol as an antiseptic in a vaccine containing Pfeiffer's bacillus, Friedländer's bacillus, streptococci, staphylococci and *B. septus*, and on the use of 0·5 per cent. phenol alone for the same vaccine. Five ml. of each were exposed to a dusty atmosphere for periods of ½ hour, 1 hour and 12 hours. The former was sterile after 12 hours, the latter after ½ hour, and showed scanty growth of staphylococci after 1 hour, and heavy growth of staphylococci and other micro-organisms after 12 hours. This experiment demonstrates the enhanced antiseptic effect obtained by the addition of a small quantity of parachlorometa-xylenol, and suggests that it is worthy of further trial in vaccines and other bacteriological products. D. R. W.

Toxicological

Toxicological Detection of Zinc Phosphide. F. Haun. (*Z. Unters. Lebensm.*, 1936, **72**, 307–312.)—Zinc phosphide has recently been employed as a means of combating domestic and agricultural pests, such as rats, mice and crows, and a number of preparations for this purpose are on the market. The commercial phosphide occurs as a grey, sintered mass, stable in air and transformed by heat into zinc phosphate. It is insoluble in water. By the action of dilute mineral acids or acetic acid upon it, phosphine is liberated, and cold conc. nitric acid decomposes it with explosive violence. A sample contained 19·17 per cent. of phosphorus and 71·03 per cent. of zinc, but, as this composition does not correspond with the composition of any one of the known pure phosphides of zinc, it is probable that a portion of the zinc is present as oxide or phosphate, or that the substance is a mixture of the different phosphides of zinc. The substance is used mixed with cattle food, especially with wheat, bran or carob bean. Occasionally, it is mixed with meat with which "blown" eggs are filled to serve as a bait for crows. The wheat product is sometimes coloured red, but when unstained it has a black, corroded appearance. For white mice one grain of the wheat preparation was found to be insufficient, but two grains caused death within twenty-four hours. With birds no specific indication of its presence appeared in the crop, but on dissecting the carcase, the odour of phosphine was usually apparent. This odour, occurring in the stomach, affords a strong presumption that death is due to zinc phosphide poisoning, and with a little experience the odour is readily distinguished from that of arsine. The pharynx is usually inflamed and red. The stomach and intestines are inflamed and suffused with blood. There is inflammation of the kidneys and the liver is swollen and yellow. If the material is not highly decomposed, phosphine can be detected. If decomposition has reached an advanced stage, proof of the presence of zinc phosphide must depend upon the detection of zinc and a consideration of the symptoms. The amount of zinc found in the investigations undertaken was so small that poisoning by other zinc salts was excluded. The simplest and most rapid method for the detection of phosphine is as follows:—A few grams (5 to 10 are sufficient or, if a negative result is expected, 20 to 30 g.) are placed in a small (50 or 100 ml.) flask. Dilute sulphuric acid containing a little copper or cadmium salt is then added, and the flask is immediately closed by means of a cork stopper carrying a mercuric bromide paper. After a short time the paper is stained yellow by the phosphine evolved. Mercuric cadmium iodide paper moistened with a drop of acetic anhydride may also be used and, since the presence of hydrogen sulphide does not affect this test, the dilute sulphuric acid used needs no addition. The papers must be freshly prepared, that of mercuric bromide from a 5 per cent. alcoholic solution and that of mercury cadmium iodide from a 5 per cent. aqueous solution (Weber, *Arb. Reichs-Gesund-Amt*, 1934, **67**, 183). Methods depending upon the isolation of phosphine by distillation are not recommended owing to their liability to cause explosions. Detection of zinc by precipitation as sulphide from large amounts of material is tedious. Detection by means of dithizone or by Rinmann's green is also not satisfactory. Detection with ferrocyanide involves the separation of iron and the test is not specific in the presence of manganese. Detection by means of cobalt mercury thiocyanate provides a rapid and convenient method. The reagents required are:—Cobalt sulphate solution (0·095 g. of $CoSO_4{\cdot}7H_2O$ in 100 ml. of $N/2$ hydrochloric acid), alkali mercury thiocyanate solution (8 g. of mercuric chloride and 9 g. of ammonium thiocyanate in 100 ml. of water, allowed to stand for a few days) and solid alkali fluoride. A portion of the material (5 to 10 g., or 20 to 30 g. if a negative result is expected), is mixed with some sodium carbonate and ignited. The residue is acidified with hydrochloric acid, and the solution is evaporated to a small bulk and poured off from any large amount of sodium chloride which separates. The solution to be tested must be neutral or only faintly acid. One or two drops of the solution are mixed with one or two drops each of the mercury and double thiocyanate cobalt solutions in the depression of a porcelain tile. If a red colour (due to iron) develops in one or two minutes, a milligram of solid alkali fluoride is added and will cause its disappearance. The mixture is then stirred, and the sides of the vessel are rubbed with a glass rod for 15 seconds. Immediately, or in not more than two minutes, a blue precipitate forms. Subsequent formation of a blue colour is not specific for zinc. A control experiment should be carried out with a drop of pure water. The cobalt solution will give a blue colour when allowed to stand for a long time after addition of the mercury thiocyanate solution, but this colour appears immediately in the presence of very small amounts of zinc.

A. O. J.

Agricultural

Cacao Shell and Its Use as an Accessory Fodder. A. W. Knapp and A. Churchman. (*Chem. and Ind.*, 1937, 56, 29–33.)—The present paper brings previous work up to date (*cf.* ANALYST, 1919, **44**, 2; *J. Soc. Chem. Ind.*, 1918, **37**, 240). In 1935 the total available cacao shell, based on the yield of 10·5 lb. from 100 lb. of beans, is estimated at 65,000 tons, of which 8,000 tons were produced in Great Britain. Analysis of five commercial samples of large shell gave the following results:

	1	2	3	4	5
Moisture, per cent...	4·6	6·7	7·8	7·0	10·9
Petroleum spirit extract, per cent.	3·0	3·1	2·5	4·3	4·2
Zeiss refractometer reading of fat at 40° C.	57	61	57	56	63
Ash, per cent.	12·4	8·4	7·9	7·3	9·0
Theobromine on dry shell, per cent.	1·26	1·55	1·69	0·80	0·98

The fuel value of the shell is about 8000 B.Th.U. The gas obtained is equivalent in power to ordinary producer gas, but the main uses of the shell are as an ingredient in cattle food and, to a less extent, as a fertiliser. It should not be used as a cheap innocuous filler or appetiser in cattle food, but with due regard to its peculiar properties. The complete analysis of a commercial roasted large shell is as follows in percentages:—Water, 3·8; fat, 3·4. Ash: total, 8·1; water-soluble, 3·5; water-insoluble, 4·6; silica (*i.e.* acid-insoluble), 1·1; alkalinity (as K_2O), 2·6; chlorides (as salt), 0·07; iron (Fe_2O_3), 0·03; phosphoric acid (P_2O_5), 0·8; copper, 0·004. Nitrogen: total nitrogen, 2·8; protein nitrogen, 2·1; ammoniacal, 0·04; amide nitrogen, 0·1; theobromine, 1·3; caffeine, 0·1. Carbohydrates: sucrose, nil; glucose, 0·1; starch (by takadiastase method), 2·8 (no true starch); pectins, 8·0; fibre, 18·6; cellulose, 13·7; pentosans, 7·1; mucilage, 9·0. Tannins: acetone-soluble, 1·8; tannic acid (Löwenthal), 1·3; cocoa red, 2·0. Acids: acetic (free), 0·1; citric, 0·7; oxalic, 0·32. Extracts: cold water, 20·0; alcohol, 10·0. A general analysis of cacao shell compared with meadow hay is as follows:

	Cacao shell Per Cent.	Meadow hay Per Cent.
Dry matter	95·45	84·0
Protein	16·07	13·5
Fat	4·62	3·0
Carbohydrates	47·56	40·5
Crude fibre	18·23	19·3
Mineral salts	7·92	7·7
Theobromine	1·03	—

Following the experimental feeding experiments carried on at Reading University and the satisfactory results obtained therefrom, the shell has now been fed to two herds of cows (28 and 25 head) producing Grade A milk, 2 lb. per day being given to each cow for a period of approximately 7 months from October 4th, and continued after the cows were out at grass. The cows all showed a liking for the shell, no scouring occurred—in fact rather the reverse—and the shell was found to store satisfactorily. As with the Reading tests, there was a distinct tendency to an increase in butter-fat in the milk, and this was noticeable when comparing with results on the control farms. Also cacao shell has a high vitamin *D* potency (ANALYST, 1936, **61**, 350), at least a quarter that of cod-liver oil. The importance of keeping to a 2-lb. ration is emphasised, since the theobromine is a stimulant. This quantity enables the farmer to obtain full value from the digestible constituents of the shell. D. G. H.

Organic

Rapid Qualitative Detection of Nitrogen in Organic Substances. H. Gauduchon-Truchot. (*Ann. Chim. anal.*, 1936, **18**, 316–317.)—To a little of the substance contained in a test-tube is added 1 ml. of pure sulphuric acid. The liquid is heated to boiling and dilute perchloric acid (66 per cent. perchloric acid diluted to one-third strength) is added, drop by drop, until decolorisation occurs. The tube is then cooled in running water, an excess of sodium hydroxide solution is added, and ammonia is tested for by litmus paper or paper saturated with Nessler reagent placed in the mouth of the tube. In tests with pyramidon only a few minutes' heating with the sulphuric-perchloric acid mixture were required for decolorisation, which was quicker by the use of the dilute than with strong perchloric acid. Positive tests for nitrogen were obtained with a wide range of organic nitrogenous compounds. S. G. C.

Determination of Nitrogen in Kuznetzky Basin Coals by Formol Titration. T. M. Slobodskaya. (*Zavodskaya Laboratoriya*, 1936, 600–601.)—Coal is decomposed by the Kjeldahl process, the residue is transferred to a conical flask, diluted with water to 150 ml., roughly neutralised in presence of methyl red, with 30 per cent. sodium hydroxide solution, and, after removal of carbon dioxide by boiling, neutralised accurately with $N/10$ and acidified with 3 drops of $N/10$ sulphuric acid. Twenty ml. of formalin neutralised to phenolphthalein are added, and the liquid is titrated with $N/10$ sodium hydroxide solution. The number of ml. of sodium hydroxide solution, multiplied by 0·0014, gives the weight of nitrogen in the sample. The reaction is expressed by the following equation:—

$$2(NH_4)_2SO_4 + 6HCHO = (CH_2)_6N_4 + 6H_2O + 2H_2SO_4$$

S. P. S.

The Triene Acid from Seeds of Pomegranates. E. H. Farmer and F. A. Van den Heuvel. (*J. Chem. Soc.*, 1936, 1809–1811.)—Punicic acid was extracted from seeds of pomegranate by disintegrating the seeds in a mincing machine, extracting with ether, evaporating off the solvent, saponifying the fat with alcoholic potash, and converting the liberated fatty acids into their magnesium salts, as described by Toyama and Tsuchiya (*J. Soc. Chem. Ind., Japan*, 1935, **38**, 182B, 185B; Abst., ANALYST, 1935, **60**, 570). The portion of the magnesium salts most soluble in alcohol yielded a solid acid which, after two re-crystallisations from 80 per cent. alcohol and one from petroleum spirit (b.p. 60°–80° C.), followed by thorough drying, melted at 44° C. It contained carbon, 77·25 per cent., and hydrogen, 10·5 per cent., the calculated figures for the acid $C_{18}H_{30}O_2$ being 77·6 per cent. and 10·85 per cent., respectively. The acid had neutralisation value 201·0 (calculated for elaeostearic acid, 201·7), and iodine value (Wijs), 217·5 (calculated, 273·7). It yielded no maleic anhydride derivative, and was converted into β-elaeostearic acid by exposing it in 10 per cent. solution in xylene, in contact with a little sulphur and in an atmosphere of nitrogen, for 4 hours to the light from a mercury-vapour lamp. The acid was hydrogenated to stearic acid, and on oxidation with permanganate yielded a mixture of azelaic acid, oxalic acid, and valeric acid. With α-elaeostearic acid it gave a eutectic point of 35° C., and with β-elaeostearic acid a eutectic point of 38° C. The claim of the Japanese authors (*loc. cit.*) to have isolated a third (doubtlessly geometrically isomeric) form of elaeostearic acid is therefore substantiated. E. M. P.

Determination of Hydroxylated Acids of Fats. P. G. Hofner, R. H. Swinney and E. S. West. (*J. Biol. Chem.*, 1936, **116**, 691–697.)—Samples for analysis are weighed into two dry reaction tubes (0·5 to 1·0 g. of materials with high acetyl values and 1·0 to 1·5 g. of those with low values). In one tube are placed 5·0 ml. of the acetylating mixture, and in the other 5·0 ml. of pyridine. A third tube is charged accurately with 5·0 ml. of the acetylating mixture alone. The condensers, carefully filled with water and dry on the outside, are suspended in the reaction tubes, which are then placed in the holes of the steam-bath and heated for 1¼ hours. The condensers are then slightly raised, and 5 ml. of water are added to each reaction tube; the condensers are replaced and the tubes are heated 15 minutes longer, with occasional careful shaking. After cooling, the condensers and the reaction tubes are rinsed down with 15 ml. of butyl alcohol, and the solutions are titrated with the alcoholic alkali, 4 drops of 1 per cent. phenolphthalein solution being used as indicator. The titrations of duplicate blanks should not vary more than 0·02 ml., the end-points being very sharp. Calculations, as mg. of acetyl found per g. of sample, are based on the method of West, Hoagland and Curtis (*J. Biol. Chem.*, 1934, **104**, 627). The acetic anhydride, pyridine and butyl alcohol are as previously used by these latter authors. The alcoholic alkali is 0·5 *N* potassium hydroxide, aldehyde-free, and is prepared according to the method of Malfatti (*Z. anal. Chem.*, 1912, **50**, 692). The acetylating mixture consists of one volume of acetic anhydride and seven volumes of pyridine. The reaction tubes are (25 × 200 mm.) Pyrex test-tubes; the condenser tubes are (18 × 150 mm.) Pyrex tubes with a rubber ring under the rim. The cover of the steam-bath is made of heavy sheet metal or painted re-inforced board, and the holes are 1⅛ in. in diameter. Rubber rings are fitted near the bottoms of the reaction tubes, so that they may be placed through the holes in the steam-bath cover with the bottoms of the tubes projecting 5 cm. below the cover into the bath. The pipettes are those described by West, *et al.* A 25-ml. burette graduated in 0·05 ml. with a 20-gauge stainless hypodermic needle fitted to the tip is employed. This tip delivers 0·007 ml. of 0·5 *N* potassium hydroxide solution per drop. The authors used the titration apparatus described by West (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 62), but a hand stirrer, consisting of a small glass rod with a loop or coil at the bottom and bent at right angles to the stem, may also be used. S. G. S.

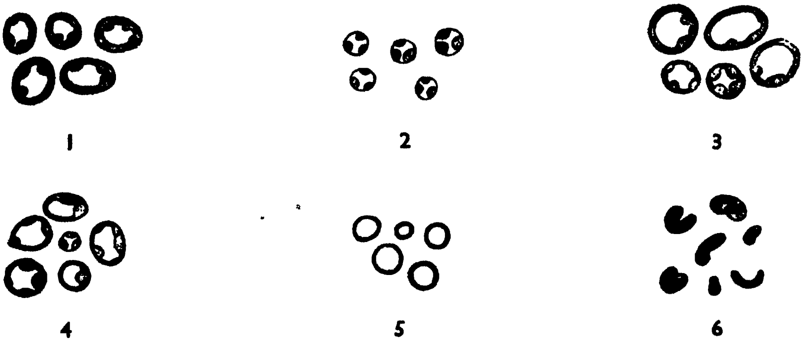
Seed Wax of *Simmondsia californica*. T. G. Green, T. P. Hilditch and W. J. Stainsby. (*J. Chem. Soc.*, 1936, 1750–1755.)—The work of Greene and Foster (*Bot. Gazette*, 1933, **94**, 826) on the liquid oil obtained from seeds of *Simmondsia californica* Nutt. has been extended. A golden-yellow oil, with saponification equivalent 604·1 and iodine value 86·3, was extracted with light petroleum (b.p. 40°–60° C.) from ground-up seed kernels. The oil was hydrolysed with an excess of alcoholic potassium hydroxide, the alcohols were separated from the solution of potassium soaps, and the acids were recovered and re-saponified in order to ensure complete hydrolysis of the wax. There were obtained 95·6 g. of acids (mean molec. equiv., 309·6; iodine value, 82·1) and 91·9 g. of alcohols (mean molec. equiv., 307·7; iodine value, 84·3). The acids were converted into their lead salts, the latter were separated into soluble and insoluble salts, and the methyl esters of the two groups of acids were fractionally distilled *in vacuo*. The two groups of acids were, for the most part, similar, except that the acids with soluble lead salts appeared to contain minor quantities (not more than 6 to 7 per cent. of the total acids) of oleic and palmitic acids. The constants of the methyl esters are given in tables. The chief acid present was identified as $\Delta^{11:12}$-eicosenoic acid, accompanied by smaller quantities of a higher (possibly docosenoic) acid.

The mixed alcohols were also fractionally distilled *in vacuo* and studied by hydrogenation and oxidation to acids and to trihydric alcohols. The results indicated that $\Delta^{13:14}$-docosenol is present, and that the other alcohol, which is present in equal or slightly larger proportion, is probably $\Delta^{11:12}$-eicosenol. E. M. P.

Determination of Thiourea. R. Cuthill and C. Atkins. (*J. Soc. Chem. Ind.*, 1937, **56**, 5–8T.)—The reaction of thiourea with silver nitrate and with various oxidising agents has been examined with a view to their utilisation in studying the sorption of thiourea from aqueous solution. In Volhard's method (addition of silver nitrate to the ammoniacal solution) the end-point cannot be precisely located, and the method was improved by adding excess of standard silver nitrate and, after reaction had occurred, acidifying with nitric acid, filtering off the precipitate, and determining the excess of silver in the filtrate by titration with standard thiocyanate. It was found that the amount of ammonia may vary within wide limits provided the amount of free acid finally present does not vary greatly. The concentration of nitric acid, other conditions remaining the same, could be varied between 2 *N* and 8 *N* without affecting the accuracy of the result, and the method was found equally accurate for all concentrations of thiourea between 0·5 and 5·25 g. per litre. Various oxidising agents were also tried. Neither potassium permanganate nor chloramine T was satisfactory. With ceric sulphate the following procedure gave good results (*cf.* ANALYST, 1928, **53**, 404):—A mixture of 10 ml. of approximately 0·025 *N* thiourea solution, 25 ml. of 0·1 *N* ceric sulphate solution and 25 ml. of 4 *N* sulphuric acid are boiled under a reflux condenser for 30 minutes and, after cooling, the excess of ceric sulphate is titrated with 0·025 *N* ferrous ammonium sulphate solution, with the use of xylene-cyanol FF as indicator (not all preparations on the market appear to be suitable). When the concentration of thiourea falls below about 1 g. per litre, oxidation appears not to be complete. Potassium dichromate may be used as the oxidising agent under almost the same conditions as ceric acid, and recovery was 100·8 per cent. with as small a quantity of thiourea as 0·1691 g. per litre. If iodine in alkaline solution is used, 10 ml. of approximately 0·025 *M* thiourea solution are mixed with 10 ml. of 2 *N* sodium hydroxide solution, then 50 ml. of 0·1 *N* iodine solution are added, and after 15 minutes the mixture is acidified with 20 ml. of 4 *N* sulphuric acid and titrated with 0·1 *N* sodium thiosulphate solution. Four mols. of iodine react with 1 mol. of thiourea. The method was accurate for concentrations of thiourea between 3·19 and 0·1595 g. per litre. D. G. H.

Analysis of Tanning Materials by the Use of Dry Chromed Hide Powders. J. G. Parker and A. Harvey. (*J. Int. Soc. Leather Trades Chem.*, 1936, **20**, 545–550.)—A historical survey is given of the controversy over Baldracco and Camilla's modification (*id.*, 1919, **3**, 111; 1920, **4**, 88; 1929, **13**, 365; 1935, **19**, 367) of the official "Shake Method," from which it is concluded that a dry chromed powder of standard quality giving results in accordance with the official method is commercially available, and that the proposed method is simpler, more rapid and less subject to errors. The authors therefore decided to test the effect of age on Lyons, Freiberg and Turin hide powders, which had been stored in unsealed tins, using the Baldracco method as provisionally approved, as follows:—The dry ready-chromed hide powder (6·5 g.) is shaken in the improved Darmstadt apparatus (*cf.* Parker, *id.*, 1928, **12**, 520) with 75 ml. of the tannin solution to be analysed, for 15 minutes, in a mechanical shaker rotating at 50 to 60 r.p.m. The partially detanninised solution is separated with the aid of a vacuum pump, and the procedure is repeated on a further 75 ml. of tannin solution, with shaking for 20 minutes. The detanninised solution is then collected in a dry beaker, 50 ml. are evaporated to dryness, and the residue is weighed. The Darmstadt apparatus consists of a glass crucible to which a cap may be attached by springs, so that the liquid it contains may be shaken and subsequently filtered by attaching the crucible to a filter-flask. Comparisons of the results obtained (in 42 tests with 15 different tanning agents) for the above-mentioned three hide powders and by the official method showed that dry pre-chromed hide powders give results in agreement with those obtained by the official method, even if the powders have been stored for 3 to 6 years and are derived from different sources (*cf.* Stather, *id.*, 1935, **19**, 370). J. G.

Recognition of Akon- (Akund-) Vessels in Kapok. N. J. M. Vorstman. (*Chem. Weekblad*, 1936, **33**, 746–747.)—The conclusions of Dingemans (*id.*, 1936, **33**, 8) are criticised. Thus, the colour-reaction with a solution of phloroglucinol in hydrochloric acid is unreliable, because a sample of genuine Java kapok gave such a strong red colour that it might easily have been mistaken for akon, whilst different types of akon gave colours of varying intensity which were so weak in some cases as to be misleading. The safranine and neocarmine stains were even less satisfactory. The longitudinal markings, which are characteristic of akon, may be rendered visible under the microscope by racking the objective up and down. According to Dingemans, the single hairs are usually silky with thin walls, and there are 2 to 5 longitudinal markings with reticular cross-connections. The influence on this test of the presence of an air-bell is discussed, and in this connection cross-sections of the vessels were cut from samples of the fibres embedded in collodion. Figs. 1 to 6 show, respectively, Bombay akon (*Calotropis procera*), Widoeri (*C. gigantea*), a commercial sample alleged to be kapok but really akon, commercial akon (containing Widoeri), genuine kapok, and cotton (for comparison,



(1) Bombay akon (*Calotropis procera*). (2) Widoeri (*Calotropis gigantea*). (3) Commercial "kapok" (akon). (4) Commercial akon (widoeri admixture). (5) Kapok. (6) Katoen (cotton).

as no lumen is visible). The circular section and uniformly thin walls are characteristic of all types of kapok, and the longitudinal markings of akon are plainly visible as 2 to 4 irregularities in thickness in the walls; these are frequently spaced at regular intervals around the periphery (*cf.* Hansma, *id.*, 1936, 33, 620, 624).

J. G.

Inorganic

Detection of Manganese. N. A. Tananaeff. (*Z. anal. Chem.*, 1936, **107**, 343–347.)—The solution to be tested (2 to 3 ml.) is neutralised with alkali hydroxide until slightly cloudy, and treated with a moderate excess of potassium cyanide. The cyanides of a number of metals re-dissolve, whilst the hydroxides of aluminium, chromium, lead, and bismuth are precipitated. Sodium peroxide in small portions is added to the solution, which is heated to boiling; aluminium, chromium, and lead dissolve, whilst manganese dioxide is precipitated. Bismuth hydroxide remains insoluble, but does not vitiate the test. If bismuth preponderates, the cyanide solution may be filtered prior to treatment with peroxide. Steels and cast iron are dissolved in nitric acid, the iron is precipitated with zinc oxide, the solution is boiled and filtered, and the filtrate is tested as described above. The test detects 0·0001 g. of manganese in 4 ml. of solution. W. R. S.

Colorimetric Determination of Titanium in Presence of Bromide. D. Lewis. (*Z. anal. Chem.*, 1936, **107**, 408–409.)—Bromide is oxidised in acid solution by hydrogen peroxide, whereby the solution becomes coloured; hence bromide interferes in the colorimetric determination of titanium. The interference can be overcome without additional manipulation by treatment of the solution with acetone, a colourless bromine substitution product being formed. The solution to be tested is treated with 30 ml. of 12 *N* sulphuric acid, 3 ml. of 3 per cent. hydrogen peroxide and 5 ml. of pure acetone, and diluted to 100 ml. The colorimetric determination is then carried out as usual. W. R. S.

Determination of Potassium as Cobaltinitrite. L. Jendrassik and A. Polgár. (*Z. anal. Chem.*, 1936, **107**, 417–420.)—The authors find the cobaltinitrite method to give accurate results provided that the precipitation is carried out as described, not with a stock solution of the precipitant. The precipitate is dissolved in strong sulphuric acid, and the nitrite is determined volumetrically. The solution (10 ml., containing 0·002 to 0·01 g. of potassium) is treated with 5 ml. of 25 per cent. cobalt sulphate or nitrate solution, 10 ml. of 50 per cent. sodium nitrite solution, and 5 ml. of acetate mixture (2 parts of strong sodium acetate solution to 1 part of acetic acid). Two blank tests are made with 10 ml. of water. The beakers are left in the cold for 5 to 18 hours, and the precipitates are collected under gentle suction on asbestos supported by a perforated porcelain plate. The asbestos filter should be purified before use by successive treatments with water, 10 ml. of strong sulphuric acid, 10 to 30 ml. of 0·005 *N* permanganate solution, the same quantity of *N* sodium hydroxide solution, and finally with water. Precipitate and beaker are washed with 50 to 70 ml. of water. The funnel is then transferred to another suction flask containing 200 ml. of water and 20 ml. of 0·1 N permanganate solution. Strong sulphuric acid (10 ml.) is added to the funnel, and 3 ml. to the precipitation beaker. When the precipitate has dissolved, the acid is drawn into the suction flask. The filter is washed with the 3 ml. of acid from the beaker, then twice with 3 ml. of 50 per cent. sulphuric acid, and then with water. The permanganate solution is left to cool for a few minutes, treated with 5 ml. of 15 per cent. potassium iodide solution, and titrated with 0·1 N thiosulphate. The blanks are treated in the same manner, the asbestos filter being available for use again after an intervening treatment with acid permanganate solution, caustic alkali, and water. The difference between the blank reading and the assay is multiplied by 0·6515 (the stoichiometric factor for potassium), giving the quantity in mg. The mean error in 22 determinations of 0·008 g. of potassium was 0·02 per cent. With 0·002 to 0·004 g. of metal the error did not reach 0·3 per cent. W. R. S.

Determination of Small Quantities of Hydrogen Sulphide and Sulphur Dioxide. W. G. Gurevitch and W. P. Wendt. (*J. Obshchei Chimii*, **1936**, **6**, 962–971.)—It is shown that the oxidation of sulphites by air in ammoniacal solution is accelerated in presence of copper compounds and still more so by cobalt salts, which are nine times as active as copper salts; hydrogen sulphide, on the other hand, is little affected during the 30 minutes' period of the test. By adding lead nitrate to the acidified solution in dilute alcohol, the resulting turbidity, due to lead sulphate, is much more stable than a barium sulphate turbidity. The intensity of the turbidity is measured by means of a nephelometer, the construction of which is described. The sulphur dioxide and hydrogen sulphide are oxidised together by means of hydrogen peroxide, and the sulphuric acid produced is determined by the same turbidity method. S. P. S.

Sodium Chlorite as a Volumetric Oxidising Agent. D. T. Jackson and J. L. Parsons. (*Ind. Eng. Chem. Anal., Ed.*, 1937, 9, 14–15.)—Sodium chlorite is now available commercially as a white finely crystalline powder which is slightly hygroscopic. Its solubility is 91·3 parts in 100 parts of water at 30° C. The freshly-prepared solution is colourless, but, when exposed to light, it gradually changes to yellowish-green, and loses oxidising power. The solution was found to be entirely stable, however, if kept in a glass-stoppered bottle and protected from light. The reagent is proposed for the determination of sulphite. To the sulphite solution (100 ml.), 15 ml. of 10 per cent. potassium iodide solution, 15 ml. of 30 per cent. acetic acid and 5 ml. of 1 per cent. starch solution are added. The liquid is titrated with standard chlorite solution to the appearance of a permanent starch-iodine blue colour. A $N/10$ solution (which contains one-fortieth of the gram-molecular weight) may be standardised by addition of potassium iodide and dilute acetic acid and titration with standard thiosulphate. S. G. C.

Explosion Risks in the Use of Perchloric Acid. (*a*) **O. Hackl** (*Z. anal. Chem.*, **1936**, **107**, 385–387), (*b*) **J. Meyer and W. Spormann** (*ibid.*, 387–388.)—(*a*) Extracts from the American literature are given on the danger of explosions in evaporating, boiling, or distilling perchloric acid in presence of organic matter, *e.g.* alcohols, rubber-stoppers, or other oxidisable substances such as antimony trioxide. The passages quoted occur in Hillebrand and Lundell's *Applied Inorganic Analysis* (p. 37), Noyes and Bray's *System of Qualitative Analysis for the Rarer Elements* (pp. 32, 286), and Washington's *Chemical Analysis of Rocks* (4th Ed., pp. 236, 237). The author has used the perchlorate method for the determination of potassium in rocks and mineral waters for many years without experiencing any explosions, because he never heated or evaporated the alcoholic filtrates.

(*b*) The formation of very explosive perchloric esters has been advanced as the cause of explosions in the evaporation of alcoholic solutions of perchloric acid, but such ester formation is possible only in the absence of water. The explosions must be due to spontaneous decomposition of the acid in contact with oxidisable substances, though the mechanism of the reaction is still obscure. Whatever the cause, the evaporation of such alcoholic solutions should be avoided. Aqueous solutions of perchloric acid can be evaporated with impunity. (*Cf.* ANALYST, 1931, **56**, 686.) W. R. S.

Detection of Traces of Sulphur in Argon. I. I. Strishevsky and I. V. Korablev. (*Zavodskaya Laboratoriya*, 1936, 591–592.)—Advantage is taken of the following reactions:

1. $S + H_2 = H_2S$
2. $SO_2 + 3H_2 = H_2S + 2H_2O$
3. $SO_3 + 4H_2 = H_2S + 3H_2O$

Argon and hydrogen are passed through a Y-piece into a glass tube in which is fused a platinum capillary heated to 800° C. in an electric furnace. The gas is then conducted into an inverted funnel dipping in a 10 per cent. lead acetate solution. S. P. S.

Volumetric Determination of Selenic Acid. R. Dolique. (*Ann. Chim. Anal.*, 1936, **18**, 313–315.)—The solution (100 ml.), containing about 40 ml. of conc. hydrochloric acid (sp.gr. 1·19) for each 0·2 g. of selenic acid present, is heated nearly to boiling for 10 minutes in a flask fitted with a reflux condenser. During this time a slow stream of carbon dioxide is passed through the apparatus, the chlorine, liberated according to the reaction,

$$H_2SeO_4 + 2HCl \rightleftharpoons H_2SeO_3 + H_2O + Cl_2$$

which proceeds practically to completion, is received in potassium iodide solution, and the liberated iodine is titrated with standard thiosulphate solution. The precision of the method is stated to be about 0·5 per cent. S. G. C.

Microchemical

Spot Tests for Substances Sparingly Soluble in Acids. F. Feigl. (*Mikrochem.*, 1936, **20**, 198–208.)—Certain constituents of the insoluble residue may readily be identified: (1) *Insoluble sulphide*, such as mercuric sulphide, arsenic sulphide and naturally occurring sulphides, *e.g.* pyrites. The sulphide may be detected by catalysis of the iodine-azide reaction:—$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$. A few granules of the sample are placed on a watch-glass and covered with 1 or 2 drops of the reagent (3 g. of sodium azide in 100 ml. of 0·1 N iodine solution), and the occurrence of bubbles of nitrogen is noted. (2) *Insoluble sulphate*, such as lead sulphate, barium sulphate, strontium sulphate and calcium sulphate:—When sulphides and free sulphur are absent the sample is reduced to potassium sulphide with metallic potassium and identified by means of the azide-iodine reaction or the sodium nitroprusside test. The reduction is carried out in a small hard glass tube with a bulb. The potassium is carefully melted, the tube is heated to redness for a short time, and then broken by placing it in about 5 drops of water, The test for sulphide is carried out on the extract without filtering. Lead sulphate can be detected in the presence of the alkaline earth sulphates by stirring about 1 mg. of the sample with a warm mixture of acetic acid and ammonium acetate, which dissolves the lead as a complex acetate. The suspension is taken up on filter-paper, treated with hydrogen sulphide, when a black stain indicates lead sulphide. (3) *Silver salts*, such as silver iodide, bromide, chloride, cyanide, and thiocyanate: The test depends on the solubility of silver halides in alkali cyanides, with the formation of complex cyanides. A bright red colour or precipitate appears within half-a-minute when the insoluble sample is treated on a white spot-plate with 1 or 2 drops of the reagent prepared from freshly-precipitated and washed nickel cyanide by boiling with potassium cyanide solution in insufficient quantity to dissolve the precipitate, and filtering. This reagent, $K_2[Ni(CN)_4]$, will keep; a few ml. are mixed with a few drops of ammonia and of a saturated alcoholic solution of dimethylglyoxime immediately before the test. Silver iodide may be identified by its reaction with palladous chloride; on steaming the sample on filter-paper treated with a 1 per cent. solution of palladous chloride, a black stain is formed. (4) *Ferric oxide*:—A few grains of the sample are gently warmed with a sulphuric acid solution of potassium or ammonium thiocyanate; the characteristic blood-red colour appears. (5) *Aluminium oxide* must first be taken up by heating with alkali pyrosulphate or bisulphate. Other metals are removed from the aqueous solution by treatment with excess of alkali and centrifuging. The aluminium is then identified by the morin test or the alizarin test. (6) *Chromic oxide and anhydrous chromic chloride*:—The sample is fused with a 1:1 mixture of sodium carbonate and sodium peroxide, dissolved in a few drops of concentrated sulphuric acid, and tested with diphenylcarbazide. Spot tests may also be used to detect the following: manganese dioxide and lead peroxide, after being taken up with dilute nitric acid and hydrogen peroxide; tungstic oxide after fusion with sodium peroxide; metallic tungsten and molybdenum, after fusion with potassium nitrite; silica and silicates, after fusion with sodium potassium carbonate; antimony pentoxide; insoluble fluorides; metastannic acid and stannic phosphate, by a flame test after reduction with zinc and hydrochloric acid (Meissner, ANALYST, 1930, 60, 465). J. W. M.

Micro-estimation of Menthol, Menthone and Menthyl-esters in the Essential Oils of *Mentha*. H. Ullrich and M. Schneider. (*Hoppe-Seyler's Z. phys. Chem.*, 1936, 245, 181–184.)—The oil is obtained from the plant or drug by steam distillation in Clavenger's apparatus in a paraffin bath at 130°–140°. The time of distillation varies from 45 to 60 minutes according to the amount of material used. The original apparatus has been modified to include a micro-burette, having a scale divided to 0·001 ml., below the usual micro-burette. At the end of the distillation the apparatus is allowed to cool and, by running off the water slowly, the oil is transferred to the micro-burette and its volume ascertained. Although there is practically no loss, a correction may be necessary, and this is easily determined. The use of this method necessitates only 1 or 2 g. of material and the accuracy is equal to that with much greater amounts of material. The assay of menthol and menthone by determination of their redox potential is only applicable to chemically pure substances, as other compounds present in the oil have their own effect on the electrodes. In the determination of menthone, the hydroxylamine method of Bennett and Salamon (ANALYST, 1927, **52**, 693) is combined with Rehberg's micro-titration method (*Biochem. J.*, 1925, **19**, 270), and 0·1 *N* alcoholic potassium hydroxide is used instead of the usual 0·5 *N* solution. Menthol is oxidised to menthone with chrom-sulphuric acid, as described by Beckmann (*Annalen*, 1888, **250**, 324), and is then determined by the hydroxylamine method. For the determination of the menthyl esters, the oil is saponified on a water-bath, in a 25-ml. flask connected by a ground-glass joint with an air-condenser. The excess potassium hydroxide is titrated with 0·1 *N* sulphuric acid solution, and the amount used up is calculated to menthyl esters. Hence in an assay of peppermint oil, the menthone is determined direct as such, the menthol is oxidised to menthone which is again determined, and the ester-content is obtained by saponification. S. G. S.

Determination of Small Quantities of Nicotine by a Silicotungstic Acid Micro-method. J. R. Spies. (*Ind. Eng. Chem. Anal. Ed.*, 1937, **9**, 46–47.)—Nicotine in hydrochloric acid solution was determined thus:—A measured volume of the solution of nicotine in *N*/10 hydrochloric acid is placed in a weighed porcelain crucible with darkened interior, and an Emich filter-stick is used (*cf.* Emich, *Microchemical Laboratory Manual*). After dilution to an acidity of *N*/20, the solution is made up to 10 ml. with *N*/20 hydrochloric acid, and stirred with a short 2-mm. glass stirring rod while 0·1 ml. of a 12 per cent. solution of silicotungstic acid is added. (To precipitate 0·5 mg. of nicotine, 0·2 ml. of silicotungstic acid are added.) The stirring rod is then removed and washed with a few drops of 0·005 *N* hydrochloric acid. This rod should be cleaned with warm chromic acid each day before use. The crucibles are covered and allowed to stand overnight, so that the amorphous precipitate may crystallise. The liquid is filtered from the precipitate by means of the filter-stick, and the walls of the crucible and filter-stick are washed three times with approximately 1 to 2 ml. of cold *N*/200 hydrochloric acid. Before ignition the crucibles and filter-stick are dried at 95° to 100° C. to remove excess of water, and then ignited in larger crucibles for 30 minutes in an electric muffle at 650° C., cooled for 2 hours in a desiccator without drying agent, allowed to stand for one hour on a metal block within the outer case of a Kuhlmann microchemical balance, and finally weighed after standing for 5 minutes on the balance pans. After weighing they are ready for another test, without removal of the residue, but it is essential to remove all loosely adhering particles from the filter-stick by tapping it against the crucible wall before removal. Platinum-tipped forceps are always used for holding the crucible. Since the crucibles are weighed on different days, the usual glass lead-shot counterpoises are replaced by counterpoises of the density of the crucible (*e.g.* porcelain crucibles) to compensate for changes in pressure, density and humidity. For general use, it is convenient to scratch a mark on the inner wall of the crucible to indicate a volume of 10 ml. Solutions containing 0·1 to 0·5 mg. of nicotine were thus analysed with an average accuracy of ± 0·002 mg. It is necessary to make a correction (0·001 mg. per ml. of *N*/20 hydrochloric acid) for the solubility of nicotine silicotungstate. Precipitations have also been made in concentrations of acid up to *N*/10, with appropriate corrections for solubility. It is advisable to modify the acid concentration according to experimental conditions.

E. B. D.

Colorimetry with a Photo-electric Cell. P. Krumholz. (*Mikrochem.*, 1936, **20**, 227–235.)—Micro-colorimetric measurements are rendered much more accurate by the use of a photo-electric cell. Cells to hold small volumes of the coloured liquid are T-shaped, so that for the observation of a layer 20 mm. in thickness, about 1 ml. of the solution is required. By means of a lens-system the maximum amount of light from the source passes through the solution, and so to the photo-electric cell, the current of which is read on a micro-ammeter (measuring about 50 micro-amps. at 1700 ohm resistance). The sensitivity of the apparatus is regulated by varying the current through the lamp source of light. Schott's colour filters are used to filter the light for the different solutions, and for each measurement the filter that gives the maximum absorption is selected. Measurements of coloured solutions containing a few γ of the substance to be determined were made with errors of the order of 2 per cent. The apparatus is obtainable from P. Haack, Vienna.

J. W. M.

Physical Methods, Apparatus, etc.

Application of Ultra-Violet Rays to Milling Products. H. Kühl. (*Mühlenlaboratorium*, 1936, **6**, 146–150.)—The beneficial effects which, it is alleged, irradiation by ultra-violet light of short wave-length produces on foodstuffs (*e.g.* milk) and water, suggest that the method may also be useful for bakery products (*cf.* Boner, *Mühle*, 1932, **69**, 646, 692; Owen, *Food Ind.*, 1932, **4**, 208). The author, however, thinks that this is unlikely, principally because bread, flour and grains of corn, etc., are solid materials, whereas the other products treated are mainly liquids, and therefore can be irradiated more efficiently. In connection with the well-known lethal effect of the radiations on certain growing organisms and insects (*e.g.* mites), the author confirms the fact that the surface colonies in a Petri-dish culture are destroyed more rapidly than those beneath. This may be due to ozonisation of the air by the radiations, or to the medium absorbing the radiation and so protecting the colonies below it. Chemical changes, beneficial and otherwise, may also be produced by the radiations, the browning of oak in sunny climates and changes in the chemical composition of the fatty matters of milk being instances of this; this effect is quite distinct from the activation of anti-rachitic principles also produced in the latter case, and it is the basis of so-called "conditioning" processes for wheat. When seeds of wheat and vetch were exposed on a moist filter-paper to sunlight (behind window-glass) and to filtered ultra-violet light for 10 hours, germination was more rapid and stronger with the latter treatment; seeds which would not germinate in the sun could not be induced to do so by exposure to the ultra-violet light. Attempts were then made to destroy moulds or prevent mould-formation, natural moulds and specimens inoculated with *Penicillium glaucum* being used, and the seeds rolled slowly down an inclined plane so that the whole surface was exposed to the radiation for 2 to 5 minutes. Subsequent culture experiments on milk agar showed that the effect of the radiation had been negligible, and although better results were obtained using fine flour, they were still considerably inferior to those recorded for liquid food-products. It is concluded that the beneficial effects of the radiation are probably due to ozonisation, and that this can be produced more cheaply and conveniently by existing electrical methods. J. G.

Electrotor Dust and Smoke Meter. S. C. Blacktin. (*J. Ind. Hyg.*, **1936**, **18**, 583–594.)—In selecting instruments for measuring the dust-contents of gases it is necessary to compromise between extreme accuracy so far as enumerating efficiency is concerned on the one hand, and speed, portability and general convenience on the other; as a rule, the latter considerations are the most important. The instrument described meets these requirements, but restricts as little as possible the range of concentration of dispersed articles that can be recorded and counted. It consists essentially of a pump (capacity 100 ml.), the plunger of which is moved by a hollow rod, whilst meshed vertically through the centre of the free face of the plunger is a length of archimedean screw which can thus revolve in and pass in or out of the hollow plunger-rod when the plunger is in motion. Attached to the archimedean screw is a celluloid or ebonite disc which revolves with the screw and thereby becomes electrified (by frictional rubbing) at the same time as the stream of the gas to be tested is set in motion by the action of the pump, the two effects being synchronous. As the incoming gas strikes the rotating electrified surface the dispersed particles are attracted to the disc, and as soon as they come into contact with it they are subjected to centrifugal force. The arrangement is such that the disc is being electrified whether the pump is being charged with the sample or discharged through the outlet valve provided, so that the electric field remains bound between the surfaces in sliding contact, including the portions of the surface of the disc where the record is not itself laid. The nature of the record is controlled by means of a stationary perforated nipple, the face of which is parallel to the disc. In this way the dirt in the air entering through the holes is deposited on the rotating disc in a regular manner in the form of concentric rings, the nature and width of which depend on the diameter of the holes, the nature of the sample and the volume analysed; the centrifugal force, moreover, aids the deposition of the particles according to size. The range of the instrument is increased by varying the number and positions of the ingress holes, and this is facilitated by means of a rotatable disc which slides over the upper face of the nipple in close contact with it, and is perforated with holes in the same relative positions as those in the nipple; various total record areas (*e.g.* from 0·12 to 24 sq.mm.) are therefore obtainable, by altering the angle through which the disc is turned. This device enables countable deposits to be obtained from heavy smoke or dust dispersions from 15 to 1,500,000 particles per ml., one stroke of the pump (occupying about 2 seconds) being adequate in every instance. The simultaneous use of several graded record areas on the same disc also enables rough comparisons of different samples to be made. Transparent or opaque discs are used according to the nature of the smoke, and these may be cleaned and re-used, or else trimmed and mounted and preserved on microscope slides 1 inch in width. Counting is carried out under the microscope on the most suitably-spaced deposit, and provision is made for deposition-areas up to 2 sq.mm., per ml. of gas analysed. J. G.

Obtaining from Mine Air Dust Particles for Physical, Chemical and Petrological Examination. H. H. Watson. (*J. Chem. Met. Mining Soc., S. Africa*, **1936**, **37**, 166–188.)—In order to define completely an air-borne dust it is necessary to state the number and mass of the particles per unit volume, and their size, distribution, and chemical and mineralogical nature. It is generally agreed that the majority of particles found in the lungs are less than 5μ in diameter, and that few exceed 10μ. Dusts common to the mining industries should be evaluated by the use of a microscope having a magnification of 1500 (with a 2-mm. oil-immersion objective, and an eyepiece of magnification between ×15 and ×20). The impinger, konimeter, Owens' jet-dust counter and sugar-tube methods of sampling are critically surveyed, and it is concluded that all of them are open to objection, often serious, which makes them unsuitable for the purpose (*cf.* Green and Watson, *Med. Res. Counc., Special Rept. No.* 199, 1935; *J. Ind. Hyg.*, 1934, **16**, 29). A new method involving the use of a thermal precipitator and a salicylic acid filter (after Briscoe) is therefore described in detail. The former depends on the fact that if a hot body (*e.g.* an electrically-heated wire) is placed in an illuminated chamber containing a dust or smoke, a well-defined dust-free wedge-shaped space surrounding the hot body will become visible. Any particles of dust present follow the convection-curves set up by the body without penetrating the space, the thickness of which depends on the difference in temperature between the hot body and the surrounding air. In this way dust in air which is drawn slowly towards the wire (by means of a water aspirator) can be deposited on cover-glasses (size No. 1) inserted at the edges of the dust-free space, linear deposits of particles running parallel to the wire being obtained. The efficiency is 100 per cent. for particles up to at least 20μ in diameter, and for needle-shaped crystals (*e.g.* of asbestos) up to at least 50μ in length. The sampling-rate is 6·5 ml. per minute, and sampling may be continued for 30 minutes if necessary. The apparatus, which is portable, consists of two self-contained parts, each of which weighs 10 lbs. Provision is also made for incinerating the samples (*e.g.* to remove tarry matter) in a spirit lamp at about 450° C. for 15 minutes, and the deposits may be mounted on microscope slides for record purposes; it is also necessary to extract some mine-dusts with hot 50 per cent. hydrochloric acid for 15 minutes. The cover-glasses should be boiled with dilute hydrochloric and washed well before use. The size-distribution of the particles is determined microscopically by means of a calibrated graticule, and it is most convenient to group the particles as follows:—Up to 0·2μ; 0·2 to 0·4μ; 0·4 to 0·8μ, etc.; 4 to 5μ; and over 5μ. Frequency curves may then be plotted. The object of the salicylic acid filter is to provide a reliable and convenient method of collecting 50 mg. of dust from 50 cb.m. of air. Such filters have a low resistance to air-flow, and they filter efficiently without clogging, while the dust may be removed without alteration by dissolving the salicylic acid in alcohol and centrifuging. For mine-dusts the A.R. acid should be ground, and 1·2 g. placed in the form of a pad in a shallow cell made from a fibre ring (thickness 0·05 inch, external diameter 5·3 cm., internal diameter 4·3 cm.) and a sheet of Whatman No. 40 filter-paper or a stainless-steel gauze (120-mesh). The paper or gauze is supported on a 20-mesh gauze, and the whole cell is held in an ebonite filter-holder and secured with a screw clamp. Before and after the test the top of the cell is covered with a sheet of cellophane (less than 0·001 inch thick), held in position by a rubber band. Three such cells are used in parallel, the sampling-rate (about 120 litres per minute) being measured by means of an ordinary household dry-gas meter (Smith high-capacity type) inserted between the compressed air ejector used to produce the suction, and the cell. The improved ejector described produces an under-pressure of 17 cm. of mercury with a maximum ejecting-capacity of about 600 litres per minute, air at a pressure of 60 lbs. per sq. inch being used. Full practical details are provided.

J. G.

Reviews

THE EXTRA PHARMACOPOEIA. (MARTINDALE.) Vol. I. Twenty-first Edition. Pp. 1072, Index pp. 109. Published by The Pharmaceutical Press, London. 1936. Price 27s. 6d.

The publication, in fifty-four years, of twenty-one editions of a work which has to be kept up-to-date, must be a record for anything of a scientific or technical character. The Martindales, father and son, gave between them, for fifty years, the personal attention and unique experience which yielded edition after edition of a book that became indispensable to the medical profession and to pharmacy; after their deaths, the work of revision had outgrown the abilities of one man, and so the Pharmaceutical Society took over the preparation of fresh editions, and, thanks to a Revision Committee and a competent editor, a new and comprehensive volume has just been issued. This Committee is comprised entirely of pharmacists, and the absence from it of any qualified medical practitioner does not appear to have caused any deficiency in the information on what, for want of a better term, may be called medical technique. It is a testimony to the fact that pharmacy is not only the hand-maid of medicine, but is willing and able to devise and give the needful *materia medica* in suitable forms for the use of physicians and surgeons.

This new edition differs slightly in size and arrangement from its predecessors, but the most noticeable and useful feature is its comprehensive index, which contains some thousands of references, including a great number to the other volume of "Martindale" (1935).

The attention of everyone will be struck by the tremendous number of names of proprietary preparations used by the medical profession, and on consulting the pages their composition will be found, in most cases, in the actual words of the manufacturers. These do not consist of the so-called patent medicines, but of the "ethical" combinations whose properties are not for general broadcasting to the public, but are only ordered by the physician; with the continued increase of such preparations it seems imperative that every medical practitioner should possess this new "Martindale," and if the pharmacist is to be prepared to deal with modern prescribing, he, too, cannot afford to be without it.

The general arrangement of some of the subject matter is certainly more convenient than extending the number of headings, but it is only made possible by reference to the comprehensive index. For instance, it seems unusual to find such drugs as Bryony, Corydalis, and the alkaloid Bulbocapnine under the heading of Aconite, or Yerba Santa, Grindelia and Phytolacca classified with Ipecacuanha.

The sections dealing with Organic Arsenic Compounds and Barbitone (and the Barbiturates) are particularly informative, and mention all the numerous derivatives marketed under different fancy names, as well as their descriptions and properties.

Thyroid and its preparations have always received special attention in "Martindale." This has been continued and brought up-to-date, and the sections dealing with Oestrin, Insulin, Gland Products, Vaccines, Sera, Toxins and Antitoxins are now more complete than anything published elsewhere in such an accessible form.

The 1935 Poisons Rules are dealt with very fully, for now that medical practitioners, as well as dispensing pharmacists, have to conform to regulations, it is necessary for a doctor, or an analyst, to know the conditions under which poisons may be dispensed for patients, or under what restrictions they may be purchased or sold.

Useful summaries of the Therapeutic Substances Regulations, 1931, and of the Dangerous Drugs Consolidated Regulations, 1928, are presented in such a way as to make them easily understood—by no means an easy task. One of the most useful sections for reference is a comprehensive Therapeutic Index of Diseases.

In its modified form the book remains the "Martindale" to which we have become accustomed during so many years. The type is excellent, the proof-reading must have been truly rigorous and effective, and the resulting book will become a tribute to the Revision Committee and editor, for it has continued all that was good in former editions and added to it a vast amount of entirely new information of particular value to pharmacists, analysts, and physicians. C. E. SAGE

"ANALYTICAL CHEMISTRY" BASED ON THE TEXT OF F. P. TREADWELL. Translated, enlarged and revised by WILLIAM T. HALL. Volume II, QUANTITATIVE ANALYSIS. Eighth Edition. Pp. 858. New York: John Wiley & Sons; London: Chapman & Hall. 1936. Price 30s.

"Treadwell and Hall" has become one of the chief analytical classics in the English language, and, as such, a new edition is, perhaps, to be judged by not quite the same standards as, say, a first edition of a new book. Originally written, apparently, as a text-book for students, it has acquired a probably unintentional reputation as a kind of inorganic "bible" to which one could turn in moments of difficulty. Whether these rôles are compatible is questionable; it is very obvious that what would be very excellent training for a student, combining diverse analytical operations in a number of separations drawn from widely different fields of inorganic chemistry, might easily be sheer exasperation and waste of time for a harassed analyst striving to get accurate results with the least possible expenditure of time and trouble for himself. As a laboratory manual for the practising analyst it has much to recommend it, much also that one would like to see altered. A notable weakness is that, amongst the multitude of methods given, there is an almost entire lack of critical data for assessing their relative merits; occasionally a process is said to give "accurate" results, though what degree of accuracy is never stated. Good, bad or indifferent, they stand shoulder to shoulder, and means of discrimination are not provided. A good example of this point occurs in the directions for standardising thiosulphate (p. 599); the first method given is with copper wire and is nothing more nor less than the ordinary iodimetric copper titration. Now it has been known for a long time that this reaction is not quite stoichiometric, and that the standardisation of thiosulphate in this way, though excellent for copper titrations, is slightly inaccurate for other purposes (*cf.* Foote and Vance, *J. Amer. Chem. Soc.*, 1935, **57**, 845). The second method given is with iodine, and here the meticulous "Treadwell" reasserts itself, and we are told not only to sublime but to resublime the iodine, and, furthermore, to cool it in a desiccator, the cover of which must not be greased and which must contain calcium chloride and not sulphuric acid. Pride of place being given to the copper method, the unwary chemist might well assume that this method, which has also the great merit of saving him a lot of time and trouble, is the one to adopt. If only a series of results obtained by every process could be given, the value of this undoubtedly valuable book would be increased enormously, and, in view of the number of students who must be constantly working through it, these results ought not to be difficult to obtain. There are many excellent processes, excellently described—in fact, clearness of description is a strong point throughout; on the other hand, there are some separations (chiefly relating to the analysis of technical products) which are distinctly crude, and one wonders why they have been included, as they seem to be rather off the beaten track for students and to be valueless for practising analysts. Even for students it seems a doubtful, though by no means uncommon, policy to force them through an impracticable scheme of analysis merely for the sake of the chemical facts they may pick up by the way.

The arrangement of the book strikes an analyst as extremely peculiar, but is probably due to the fact that its *raison d'être* is essentially teaching; it is hard to see, for instance, why a detailed description of the analysis of white lead (with one line about the determination of carbonate) should occur (pp. 347–8) in the middle of a section dealing with carbon dioxide; or why the spiritual home of a number of separations, *e.g.* iron, aluminium and phosphoric acid (p. 117) should be under the heading "Uranium." The preface states that "so many changes were made in the text that it was found best to reset the whole book"; this being the case, it is a great pity that much that is obsolete on the one hand, or of a rough "works analysis" type on the other, was not discarded. This especially applies to the section on gas analysis, in which the latest reference is dated 1918, and only 12 out of 70 are subsequent to 1910, the table of heats of combustion being taken from Thomsen (1882), ignoring the classical work of Berthelot (1897).

Most of the metals are adequately treated, whether or no one agrees with all the methods given, but osmium is omitted altogether, and the section on cobalt is most disappointing. Considering the extensive analytical literature of cobalt, it seems to demand more than the two pages, or rather less, that are allotted to it; especially in view of the twenty pages given to the gravimetric determination of carbon dioxide and the fact that three different variants of the Gutzeit process are described, though the hypophosphorous acid precipitation of arsenic is not mentioned. On the other hand, it is refreshing to see so much space given to Dr. Schoeller's work on tantalum, etc.

With its various faults, however, "Treadwell" remains an outstanding text-book, and one which has gained considerably in passing into this new edition. Its value lies not merely in its description of processes—though most of these are sound and some very recent—but also scattered through its pages there are frequent comments whose broad analytical sanity is as praiseworthy as it is rare in such books. Specially noteworthy is the discussion on the separation of arsenic, antimony and tin from mercury, lead, copper, cadmium and bismuth (p. 228), and that on the precipitation of barium sulphate (pp. 411–414); there are excellent sections, too, on such subjects as membrane fillers, oxidation-reduction potential, adsorption indicators, etc.; occasionally, also, there are warnings which are too often overlooked, as, for example, that against igniting ferric hydroxide which has been washed with ammonium chloride solution (p. 99), and that against trying to reduce ferric salts completely with sulphur dioxide without first neutralising.

An analysis of the references (other than Gas Analysis) gives perhaps a clue to some of the elements of weakness in the book. Of the 593 references, there are 505 either German or American; of the 48 British references which come next, no fewer than 12 are to *The Chemical News*, mostly of a very early date, and 9 to the *Journal of the Chemical Society*; Dr. Schoeller's tantalum work accounts for another 13, leaving only 14 to cover the remainder.

The index, where tested, seems to leave a good deal to be desired; for instance, some references occur only in the author- and not in the subject-index; rhodium and ruthenium are not mentioned, and iridium only in connection with apparatus, though processes are given for their separation. Printing and production are of a high order, and very few misprints were noticed.

The book has an undeniable charm of writing, and one cannot but feel grateful for the provision, in the analysis of commercial hydrogen peroxide (p. 570), for the case (said to occur "frequently") where it contains no hydrogen peroxide at all. The new type of binding ("flexiback") appears to be very efficient in preserving the back of the book.

B. S. EVANS

SCIENTIFIC AIDS FOR THE STUDY OF MANUSCRIPTS. By R. B. HASELDEN. Pp. x + 108. The Bibliographical Society, London. 1935.

This is a book that ought to be in the hands of every specialist who has anything to do with documents, for valuable manuscripts in many libraries and museums have been severely injured, sometimes practically destroyed, owing to a lack of the knowledge contained in this work. Unfortunately, it is not designed for general circulation and sale, but it is to be hoped that an edition for this purpose will be issued. Every important library should at least know of the existence of the book.

Few, if any, writers are better supplied with material for the study of documents than Mr. Haselden, who, as Curator of Manuscripts in the Henry E. Huntington Library, California, has access to over a million manuscripts of all kinds and in all conditions. He discusses the subject of documents in a thoroughly scientific manner with accuracy, thoroughness and moderation, and avoids the unnecessary use of technical terms.

The book is beautifully printed by the Oxford University Press. It has a very complete index and is illustrated by sixteen interesting collotypes of the highest quality. As was to be expected in a work sponsored by the London Bibliographical Society, the extensive bibliographies at the end of each chapter are an outstanding and valuable feature, including foreign books and articles, and constituting probably the most complete collection of references relating to documents.

The introductory chapter discusses the procedure suggested for the general examination of a document, with six and a half pages of bibliography relating to the general subject. The second chapter treats of the care and handling of manuscripts, followed by another complete special bibliography. Chapter III is a discussion of light and colour as related to the subject, and Chapter IV treats of "Illuminants" and "Light Filters." In Chapter V the subject of microscopes and magnifiers is discussed, with special application to the subject of manuscripts. Chapter VI gives an account of the ultra-violet lamp and fluorescence, which is of increasing importance in investigating certain document problems, Chapter VII deals with photography, and Chapter VIII with measuring instruments and handwriting. The final chapter discusses examples of interesting and important manuscript problems, showing the great variety of problems that come before the examiner of documents.

Throughout this valuable work the many special instruments that are useful in the investigation of documents are described and discussed. Again and again the author lays stress upon the point that the mind of the observer is of greater importance than the instruments or process employed. "An examination of a document through the microscope," he remarks, "is useless unless the observer can correctly interpret the image of the object as seen when magnified." It is made clear that every scientific investigation is a process of reasoning and that one sees, not only with the eyes, but with the brain. ALBERT S. OSBORN

FIFTY YEARS OF FIELD EXPERIMENTS AT THE WOBURN EXPERIMENTAL STATION. By Sir E. JOHN RUSSELL and J. A. VOELCKER. Pp. 392. London: Longmans, Green & Co., Ltd. 1936. Price 21s. nett.

The Duke of Bedford and the Royal Agricultural Society in 1876 founded the Woburn Experimental Station as a means to carry out investigations that were not receiving attention elsewhere. The book is a review of the results of the work and achievements of the Station, and it has recently been published as a Rothamsted monograph.

A few years ago a somewhat similar treatise was published which gave an account of the work and researches carried out at Rothamsted Experimental Station, but, alas, Gilbert and Lawes, who had directed the Station for more than fifty years, had both passed away. In the case of Woburn Station, though sixty years have passed since its foundation, this Jubilee book has been published during the lifetime of one who has been closely identified with the work of the Station throughout the period, and who has conducted the Station experiments for a period of over forty years, Dr. J. A. Voelcker. His many friends will rejoice to know that an account of what might be regarded as Dr. Voelcker's chief life work has been published while he is still an active worker in the cause of agriculture.

After an introduction dealing with the history of the Station, some fifty pages are devoted to the residual manurial values of cake fed to animals and with the continuous growth of cereals on the same land. Comment is unnecessary with regard to these first chapters, because their importance and significance are realised by everyone who has been interested in agriculture during recent years. Then green manuring with its attendant curious crop yields is followed by many short articles on different experimental enquiries.

Any doubt as to the justification for the existence of this Station should be dispelled by a glance at the headings of the various enquiries undertaken. Experiments embrace the feeding of stock and the cropping and manuring of soils, and are of so practical a value that few farmers can justly afford to neglect the knowledge gained by them. For instance, the use of condimental foods as a supplementary food for bullocks was investigated and found to be unnecessary and of no advantage; still the sale of condiments for this purpose is often pushed and at a price ranging up to £60 per ton.

The second part of the work, consisting of about one hundred pages, is devoted to a general statistical examination of the Station results. Here monthly averages of rainfall, or of sunshine hours, or perhaps of crop yields over periods, are depicted by means of curves or columns, which nowadays are so essentially a part of the equipment of the statistician.

Few, indeed, would attempt to assess the value of the Woburn Experimental Station's results to agriculture and, therefore, the chapter consisting of comments on the bearing of many of these results on agriculture forms one of the most interesting.

On a very early page is depicted the pot culture houses of the Station, but, strangely, no mention is made of the results obtained there. The pot culture work at Woburn was originally started to carry out investigations enjoined in the Hills Bequest of £10,000 to the Royal Agricultural Society. This embodied an enquiry into the possible part played in vegetation by mineral elements other than those of which the action and influence were ordinarily known. Dr. Voelcker experimented with a large number of such elements over a period of many years, and a very considerable number of reports have been published from time to time in the Journal of the Royal Agricultural Society. It seems at least unfortunate that some summary of this long and tedious, though interesting, work has not been included in the volume under review. Hope may, however, be expressed that Dr. Voelcker will publish later a comprehensive account of this important feature of his work at Woburn.

The frontispiece is an excellent portrait of Dr. J. A. Voelcker, who has been in charge of the Woburn experiments since 1884. He and his collaborators are to be congratulated on this monograph, which will form a reminder of the Duke of Bedford and the Royal Agricultural Society, founders of the Station, and a permanent remembrance of Dr. Voelcker and his co-workers.

F. W. F. ARNAUD

AN INTRODUCTION TO COMPARATIVE BIOCHEMISTRY. By E. BALDWIN, B.A., Ph.D. Pp. xviii + 112. Cambridge University Press. 1937. Price 5s.

This fascinating book reached the reviewer with a message—a query, rather—from the Editor of THE ANALYST, whether it was yet another of those volumes "without which no biochemist is replete?" To this apparently simple question there is no simple answer, for one has in mind the *mot* of that anonymous French wit, to whom is attributed the request "Give me life's luxuries, and I will dispense with the necessities."

Dr. Baldwin opens up fascinating vistas down which the biochemist and the biologist walk hand in hand, reconstructing from analyses of blood and urine the morphology, physiology and environment of organisms known to us only as fossil remains. The concepts of uricotelism and ureotelism may be new to most analysts, but no one who reads Dr. Baldwin's 102 pages—all too few—is likely to overlook their importance. This particular aspect of comparative biochemistry is linked up with more general observations about the tonicity of blood and other body fluids and their evolutionary significance.

The answer to the Editor's question is, perhaps, after all, "Yes." This is not a text-book or, indeed, a utilitarian production of any kind. It is a luxury, but how much more welcome and stimulating than many necessities. On the chemist replete with ordinary biochemical text-books this speculative and philosophical essay will, maybe, act not unlike the glass of *fine* after a somewhat too overpowering meal.

A. L. BACHARACH

ELEMENTARY QUANTITATIVE ANALYSIS. By CARL J. ENGELDER, Ph.D. Second Edition, 1936. Pp. xiv + 270, with 12 illustrations. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 13s. 6d. net.

Since the publication of the first edition, which was reviewed in THE ANALYST (1930, 55, 356), the author has re-arranged the order of the subject-matter and has enlarged the text by the inclusion of some additional procedures, notably the analysis of hydrogen peroxide and pyrolusite and direct and indirect determinations of available chlorine in bleaching powder. A note on the use of ceric sulphate is also included.

The general excellence of the first edition is maintained, and, on the whole, the subject-matter calls for little comment. A few minor typographical errors may be pointed out. On pages 98 and 202 there are misprints for sodium and for

ferric hydroxide; on p. 20 "may be expect to lie" needs correction; and lastly, a curious phrase, "it is quite impossible and entirely too inaccurate," occurs on p. 31.

The book, as the name indicates, is intended for the use of elementary students commencing quantitative work in inorganic analysis. The manner in which the subject-matter is displayed and also the attractive and strong binding are worthy of praise.

H. R. NANJI

Publications Received

THE METABOLISM OF LIVING TISSUES. By ERIC HOLMES. With a Foreword by Sir F. GOWLAND HOPKINS. Pp. xi + 235. Cambridge: The University Press. Price 7s. 6d. net.

ENZYME CHEMISTRY. By H. TAUBER. Pp. xii + 243. London: Chapman & Hall. 1937. Price 15s. net.

SOAP: ITS COMPOSITION, MANUFACTURE AND PROPERTIES. Fourth Edition. By W. H. SIMMONS. Pp. xi + 140. London: Sir Isaac Pitman & Sons, Ltd. 1936. Price 3s. net.

LECTURE EXPERIMENTS IN CHEMISTRY. By G. FOWLES. Pp. xv + 564. London: G. Bell & Sons, Ltd. 1937. Price 16s. net.

A SCHOOL PHYSICS. By S. R. HUMBY and F. W. GODDARD. Pp. viii + 233. London: Longmans, Green & Co. 1937. Price 3s.

BRITISH CHEMICALS AND THEIR MANUFACTURERS. The Official Directory of the Association of British Chemical Manufacturers. 1937.

PRACTICAL ORGANIC CHEMISTRY. By F. C. MANN and B. C. SAUNDERS. Pp. xi + 403. London: Longmans, Green & Co. 1936. Price 8s. 6d. net.

APPLIED CHEMISTRY FOR ENGINEERS. By A. F. H. WARD. Pp. xi + 127. London: Longmans, Green & Co. 1936. Price 5s.

CHEMISCHE ANALYSEN MIT DEM POLAROGRAPHEN. By H. HOHN. Pp. vii + 102. Berlin: Julius Springer. 1937. Price RM.7.50.

CHEMICAL ARITHMETIC. By F. W. GODDARD. Pp. vii + 99. London: Longmans, Green & Co. 1937. Price 1s. 6d.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Friday, March 5th, the President, Dr. G. Roche Lynch, being in the chair.

Certificates were read in favour of Joseph John Blackie, Ph.D., F.I.C., Ph.C., Harold William Christian, B.Sc., A.I.C., Walter Edward Green, B.Sc., Norman Heyworth Law, M.Sc., A.I.C., Leonard Thornton Lowe, B.Sc., A.I.C., Peter John Markham, B.Sc., A.I.C., Hubert Alfred Parkes, B.Sc., F.I.C., Robert Charles Tranent.

The following were elected Members of the Society:—William Mitchell Cameron, James Laurence Campbell, B.Sc., Frank James Griffin, B.Sc., Herbert Clewin Griffith, Robert Edmund Richard Grimmett, M.Sc., F.N.Z.I.C., Eric Kennedy, B.Sc., A.I.C., Robert Hay McKinlay, F.I.C., John Aitken Macnair, F.I.C., Geoffrey William Martin, Enid Marian Pope, B.A., B.Sc., Archibald Rayner, B.Sc., F.I.C., William James South, Edward Taylor-Austin, A.I.C., John Ezra Woodhead, B.Sc., F.I.C., Ph.C., James Hunter Young, B.Sc., A.I.C.

The Annual General Meeting of the Society then followed, when the Hon. Treasurer presented the accounts for the past year, and the Officers and Council for the year 1937 were elected as follows:

President.—G. Roche Lynch, O.B.E., M.B., B.S., D.P.H., F.I.C.

Past-Presidents serving on the Council.—F. W. F. Arnaud, E. Richards Bolton, J. T. Dunn, Bernard Dyer, John Evans, Edward Hinks, G. Rudd Thompson, J. Augustus Voelcker.

Vice-Presidents.—A. L. Bacharach, H. E. Cox, B. S. Evans, A. R. Tankard, J. F. Tocher.

Honorary Treasurer.—E. B. Hughes.

Honorary Secretary.—Lewis Eynon.

Other Members of Council.—E. B. Anderson, P. S. Arup, W. G. Carey, S. Dixon, F. W. Edwards, S. Elliott, B. G. McLellan, A. More, J. R. Nicholls, W. H. Roberts, J. G. Sherratt, W. H. Simmons, J. B. McKean, J. R. Stubbs.

On the invitation of the Council, Professor G. Barger, M.A., D.Sc., F.R.S., gave an address on "The Alkaloids of Ergot."

SCOTTISH SECTION

The Second Annual General Meeting was held in the Royal Technical College, Glasgow, on 26th February, 1937.

The following office bearers were elected:

Chairman—J. F. Tocher, D.Sc., F.I.C.; *Vice-Chairman*—T. Cockburn; *Committee*—A. M. Cameron, A. Dargie, T. W. Drinkwater, J. W. Hawley, M. M. Love, R. T. Thomson; *Hon. Secretary and Treasurer*—J. B. McKean; *Hon. Auditors*—M. M. Herd and R. S. Watson.

The following paper was then read and discussed:—"Boron: Its Occurrence and Estimation in Plants," by Professor D. N. McArthur and K. L. Robinson, B.Sc.

NORTH OF ENGLAND SECTION

ADDRESS OF THE CHAIRMAN (MR. ARNOLD R. TANKARD)

(*Delivered at the Meeting held at Manchester, February* 6, 1937)

MUNICIPAL CHEMISTRY

In choosing a subject on which to address you this afternoon, I felt I could not do better than ask you to consider for a few minutes the important work in which we, as chemists, are engaged; and whilst I shall speak specially from the point of view of a Public Analyst and Corporation chemist, I hope my remarks will hold something of interest to most of my audience.

One of the most important duties of the Public Analyst, whether acting for a large area such as that of a County Authority, or for a more circumscribed area like the average city or town, must ever be his work in relation to the Food Adulteration Act and allied legislation applying to foods and drugs.

Few Public Analysts can be said to be satisfied with the Acts relating to foods. These Acts are hesitating and ambiguous, and consequently a local authority sometimes finds it no easy task to bring those whom they desire to prosecute within the selected section. I often wish one simply had to put the facts before a panel of intelligent consumers and let them decide the issue. Instead of that, a local authority has to prove its case, in the full legal sense, hampered by phrases such as "provided that" and "guilty knowledge," and such words as "wilfully" and "unless," in the clauses in Acts of Parliament, which are interpreted by a lawyer from what is, after all, a narrow, albeit a perfectly proper, point of view. With a simple desire to protect those who buy foodstuffs for consumption, we must surely often sigh for the perfect Statute which would do real justice to everybody, instead of merely giving bad law to the multitude! But given an interested and sympathetic local authority, much can be done outside the Acts of Parliament, which must be evoked when ordinary food and drug samples are the subjects of prosecutions. The chemical adviser to a County Council or City Corporation, which quite commonly nowadays assumes the position of a model employer, can put his authority in the position of a model consumer. These bodies everywhere have control of many large hospitals, institutions and schools, and their consumption of foods, drugs and medicines is very considerable. It is here especially that the Public Analyst, in a field where he is a specialist, can safely guide his authority; and in recommending specifications for foods, can raise their quality to standards which are definitely superior to those which he can obtain for the general public by the operation of the Food and Drugs (Adulteration) Act. The psychological effect of this work may not be immediately obvious, but it is definite, and in the end will bring about results of importance, for ultimately this procedure puts a certain pressure upon manufacturers to conform to a reasonable standard. In my area, even the hospitals on a voluntary basis have asked for help in putting their contract supplies under similar control.

"Trade custom" is often invoked under the Food Acts when a food is alleged to be deficient in nature, or in substance, or in quality; the "custom" of local authorities in asking for tenders for foodstuffs of a higher quality for its institutions may some day, if the analyst uses his opportunities, provide a strong counterblast to such poor trade customs. Thus the Public Analyst may find it difficult in some instances to recommend prosecutions in cases of unsatisfactory samples of flour, jam, lemon curd, "faced" cereals, and potted meat; but a local authority may, and often does, lay down its own requirements for these and other commodities used in its institutions. Thus pure flour, jam of high fresh fruit content, nutritious lemon curd free from starchy fillers and fatty substitutes for butter; rice, pearl barley, lentils and split peas free from mineral polishing materials; genuine potted meat and fish of high quality—all these can be obtained by local authorities possessing specifications designed to eliminate the inferior types of food products. In some instances the National Mark series of foodstuffs may be specified; a fillip can thus be given to this desirable movement, and the local authority can obtain commodities of known high quality and purity. The specifications and methods of examination contained in the various Marketing Leaflets (Grading and Marking) of the Ministry of Agriculture are also valuable as guides to satisfactory quality in respect of the commodities included in these publications.

Even those chemists who are not Public Analysts will have heard that the average fat-content of cows' milk is much higher than the limit of 3 per cent. of the Milk Regulations! My Corporation requires all milk supplied to its hospitals and institutions to contain a minimum of 3·25 per cent. of fat.

Experience leads me to think that some analysts have yet to develop less elastic consciences. Recently, a sample labelled "lemon curd," which was "Guaranteed made from the finest ingredients with eggs, butter and lemons," was found to contain a small proportion of egg and of fatty material, of which latter 75 per cent. was margarine-fat, a considerable amount of farinaceous material, an artificial dye and lemons; and the vendors were asked to amend the label, which was considered to be misleading. The analyst to the manufacturing firm replied that he considered the label to be a true and correct disclosure of the facts, and that no purchaser of the product would be prejudiced in the slightest degree. This is typical of what sometimes happens in connection with samples condemned under the Food and Drugs (Adulteration) Acts, but most manufacturers have loftier views of commercial morality. In the other sphere, if the local authority has set up standards, such products as the lemon curd mentioned have no chance of being considered when supplies are purchased for the Council's institutions. In reporting the results of the examination of samples sent with tenders for contracts, or supplied by contractors during the period of the contract, the local authority will be notified by their analyst when any product does not conform to specification, or to his standard for a satisfactory product in cases where no specification exists; and usually the analyst's suggestions are readily accepted, wherever possible, by other officials who have to make recommendations regarding these supplies, and by the Committees to which his reports are submitted. The Public Analyst should tell his authority how some foodstuffs are treated, and what are the objections to these treatments, even when there is little or no redress at law.

I believe that one of the greatest menaces to-day is the spate of advertisements, particularly in the press, relating to certain foods and medicines. "Sweet are the uses of advertisement," says the parodist on the poet's well-known lines, but the "sweets" are very badly distributed. Advertising has now been promoted, in the eyes of its devotees, to the status of a profession, and of course newspapers lose no opportunity of proclaiming the virtues and value of press advertisements. I am inclined to think, in relation to some products, that the most important ingredient is "printer's ink." Even the best-known firms of advertising experts sometimes go sadly wrong in describing the products they are employed to "puff," and we are far from a general recognition of "Truth in Advertising." Again, someone has to pay for these advertisements, and as a consequence the consumer frequently gets a product which is either of inferior quality or excessively priced. Many modern methods of advertising foodstuffs are to the prejudice of the purchaser, and I am strongly in favour of holding all makers of advertised commodities responsible for the statements in their advertisements. There are food factories to-day where cleanliness and hygienic considerations are faithfully observed, and in this way a good advertisement is often obtained. But these hygienic factors, though important, are not everything, and in some of these very factories the composition of the commodities made leaves something to be desired.

But the chemical adviser to a local authority, though he may be the Public Analyst, often performs wider duties than those embraced within the scope of the term "foods and drugs." He is usually the scientific adviser in a comprehensive sense, and as such he is frequently asked to assist in the control of the composition and quality of a wide variety of materials, where the results of chemical and physical examinations may help in selecting the best goods for their intended purpose. For it will be realised that a local authority is engaged in big business—in many instances in very big business; it employs men, directly and indirectly, in half a hundred different trades, and it buys large quantities of materials. It requires stores of all kinds of commodities, and desires to have these of a specified quality, strength and purity. Here the County Council, or Corporation, Analyst should be the prime mover in the drawing-up of many of the necessary specifications.

I have set out, in tentative form, in the lists you have before you, some of the main classes of materials for which many local authorities accept contracts (Part I), and in Part II of the list I have enumerated various other kinds of examinations frequently required of the Analyst. In this connection, the Reports made in 1934 and 1935 by the Committee on the Standardisation and Simplification of the Requirements of Local Authorities should be consulted. My lists are not, of course, complete, but they may be useful as an illustration of the scope of our work, and in revealing what a real responsibility rests on those of us who are called to undertake it, whether for a local authority, or for an industry supplying materials to a specification.

As chemists, few of us can make any claim to be in "big business," but often we are one of the "powers behind the Throne," and we may rightly feel proud of the chemical profession to which we belong.

CHEMICAL AND GENERAL SCIENTIFIC CONTROL FOR LOCAL AUTHORITIES

PART I. MATERIALS OF RECOGNISED QUALITY OR FOR WHICH SPECIFICATIONS MAY BE DEVISED

DEPARTMENT MATERIALS

General.—Coal; Coke, etc.; Fuel Oils; Petrol; Lubricating Oils and Greases; Paints, Oils and Varnishes; Soaps and other Cleansing Materials; Driers; Turpentine Oil; Floor Polishes and Oils; Waterproofed Goods; Clothing (Uniforms, etc.); Fabrics; Disinfectants; Bleaching and Antiseptic Fluids (Chlorine); General Office Supplies (Paper, Inks, Bookbinding Materials).

Engineer's.—Road and Building Materials (Tar, Bitumen, Sand, Roofing Tiles, Cement, Stone); Cement Accelerators; Rubber; Leather; Glue and other Adhesives.

Electricity.—Special Oils (Transformer Oils, etc.); Electrical Cables; Metals; Electrical Wiring.

Education.—Foods for Children's Meals; Enamelled Ware.

Housing.—Building Materials; Electric Wiring.

Water.—Metals for Fittings (Brass, etc.).

Transport.—Water Softeners; Lubricating Oils, Greases, etc.

Baths.—Medicated Soaps, etc.; Other Cleansing Materials; Disinfectants.

Health.—Drugs and Medicines; Food-medicines for Clinics, etc.; Graded Milks; Milk for Schools; Foods and Drugs; Fertilisers and Feeding-stuffs; General Food Supplies for Institutions; Disinfectants; Insecticides; Soaps, etc.; Medicated Dressings.

Parks, Allotments, etc.—Fertilisers; Lime; Insecticides and Fungicides.

Farms.—Feeding-stuffs; Fodder; Fertilisers.

Fire Brigade.—Gas-mask Materials.

PART II. CHEMICAL AND OTHER SCIENTIFIC CONTROL WORK OUTSIDE THE SCOPE OF CONTRACTS

DEPARTMENT MATERIALS

Engineer's, etc.—Boiler Feed Waters; Boiler Scales; Water-softening Control; Metals, Alloys and Solders; Corrosion Problems; Sewages and Effluents; Trades Wastes; Sewer Gases; Investigation of causes of Breakdown in Materials, etc.; Quality of Galvanised Materials.

Water.—Periodic Analyses of City Supply Waters.

Gas.—Heating Value and Purity of Gas-supply.

Baths.—Periodic Control of Swimming Bath Waters; Treatment of Bath Waters; Periodic Control of Chlorination Plants.

Health.—Food-poisoning Cases (Chemical); Determination of Lead and Arsenic, etc., in Biological Materials; Samples under Poisons and Pharmacy Act; Investigations of Nuisances (Effluents, Pollution of Streams); Safety Work in Establishments (Foul Air, etc.); Examination of suspected Foreign Eggs; Rag Flock, Flannelette, etc.

Biochemical Work.—Chlorides, Proteins and Reducing Sugars in Body Fluids; Urine Analyses; Arsenic in Hair and Nails; Arsenic, Copper, etc., in Blood; Sugar and Urea in Blood.

Development.—Water Analyses; Advice on Industrial Possibilities of Area, etc.

Farms, Parks, etc.—Analyses of Soils.

Police.—General Crime Detection; Coining Cases; Documents; Forged Notes, etc.; Blood and Other Stains; Detection of Human Blood in Stains, etc.; Hair (examination for origin, etc.); Fibres and Dust; Alcoholic Liquors (Licensing Acts); Dangerous Drugs (Cocaine, Hashish, etc.).

H.M. Coroner.—Suspected Poisoning Cases.

Port Authority.—Waters and Foods for Ships; Contaminated Food Cargoes; Disinfectants; Fumigating Chemicals, Imported Foods, for Preservatives, etc.

Miscellaneous.—Separated Refuse (Potash, etc., in); Anti-gas Precautions; Atmospheric Pollution Analyses.

Annual Report of Council

MARCH, 1937

THE Roll of the Society stands at 788, an increase of 33 over the membership of last year.

The Council regrets to have to record the death of the following members:

Sir Herbert Jackson
F. A. Mason
J. M. H. Munro
P. A. Ellis Richards
W. Rintoul
D. A. Sutherland
L. J. de Whalley

Sir Herbert Jackson, who was in his 74th year, had been elected a member of the Society in 1915. He had had a long and distinguished career on the teaching staff at King's College, London, from which he retired in 1918 with the title of Emeritus Professor, when he was appointed Director of the British Scientific Instruments Research Association. His work on glassware during the war was of outstanding merit. He received the Honour of Knighthood in 1917; an obituary notice by Mr. R. B. Pilcher appeared in THE ANALYST for February, 1937.

Munro, who died at the age of 80, had been a member of the Society for fifty years. He was for many years Agricultural Analyst to the Wiltshire County Council and to the City of Bath. (Obituary notice, ANALYST, 1937, January, p. 2.)

Ellis Richards, who died in his 69th year, joined the Society in 1894. He served on the Council in 1900–1, but he will be best remembered for his valuable and loyal service as Honorary Secretary over a period of seventeen years; this post he only relinquished when he was elected President in 1922. During his later years illness prevented him from taking an active part in the work of the Society, but to the last he continued to follow its progress with keen interest. He will be greatly missed by a wide circle of friends. (Obituary, ANALYST, 1937, March, p. 164.)

Rintoul, who died in his 66th year, was elected a member of the Society in 1908. During the greater part of his life he was connected with the manufacture of explosives, first at the Royal Gunpowder Factory at Waltham Abbey and subsequently with Nobel's Explosives Co., afterwards incorporated in Imperial Chemical Industries.

de Whalley, who died at the age of 84, had been a member of the Society for forty-five years. He attained a high position in the field of sugar technology, and was for many years Chief Chemist to Abram Lyle & Sons, Sugar Refiners. (Obituary to appear later.)

Sutherland, who died in his 75th year, had been a member of the Society since 1884 and served on the Council in 1903–4. During the greater part of his professional career he had been connected with the petroleum industry.

During the year seven ordinary meetings of the Society have been held, and the following papers have been communicated:

"The Sulphuric Acid Test for Liquid Paraffin." By C. E. Sage, F.I.C., A.M.I.Chem.E., and S. G. E. Stevens, B.Sc., A.I.C.

"The Determination of Moisture-content by Distillation with Liquids Immiscible with Water." By L. A. Warren, Ph.D., B.Sc., A.I.C.

"An Apparatus for the Determination of Small Percentages of Water and Oil." By I. C. P. Smith, B.Sc.

"The Mydriatic Effect of Cocaine and its Differentiation from the Atropine Group of Alkaloids." By K. R. Ganguly, M.Sc.

"The Effect of some Impurities in Anaesthetic Ether: Peroxides." By J. H. Coste, F.I.C., F.Inst.P., and D. C. Garratt, B.Sc., Ph.D., F.I.C.

"The Determination of Bromides in Presence of other Halides." By F. W. Edwards, F.I.C., H. R. Nanji, Ph.D., A.I.C., and E. B. Parkes, M.Sc., A.I.C.

"A New Photographic Light Filter Cell." By C. Ainsworth Mitchell, M.A., D.Sc., F.I.C., and T. J. Ward.

"A Micro-Zeisel Apparatus for Determining Methoxyl and Ethoxyl Groups." By J. J. Chinoy, M.Sc., Ph.D.

"Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates; XXXIII, General Summary and Results." By W. R. Schoeller, Ph.D., F.I.C. (work done under the Society's Analytical Investigation Scheme).

"The Determination of Betaine in Sugar Beet By-products." By J. W. Blood, A.I.C., and H. T. Cranfield.

"The Determination of Zinc in Foods." By N. D. Sylvester, M.Sc., A.I.C., and E. B. Hughes, D.Sc., F.I.C.

"The Turbidimetric Titration of Gelatin Solutions." By J. F. Morse.

"Colour Measurement of Opaque Surfaces." By E. R. Bolton, M.I.Chem.E., F.I.C., and K. A. Williams, B.Sc., F.I.C.

"The Determination of Benzoic Acid." and "The Detection and Determination of *p*-Hydroxybenzoic Acid." By F. W. Edwards, F.I.C., H. R. Nanji, Ph.D., D.I.C., F.I.C., and M. R. Hassan, M.Sc.

"The Detection of Arachis Oil in Olive Oil." By Norman Evers, B.Sc., F.I.C.

"The Enzymes of Milk, I. Notes on Kay and Graham's Phosphatase Test." By E. B. Anderson, M.Sc., F.I.C., Z. Herschdorfer, Ph.D., and F. K. Neave.

"The Determination of Cyanide in Aqueous Extracts of Road Tars." By W. G. Moffit, Ph.D., A.I.C., and E. H. Williams, B.Sc., A.I.C.

"A Rapid Method for the Determination of Triethanolamine." By C. J. Eastland, F.I.C., Norman Evers, B.Sc., F.I.C., and T. F. West, B.Sc., A.I.C.

"Some Minor Component Acids in Milk-fat and their Possible Significance." By Professor T. P. Hilditch, D.Sc., F.I.C.

"The Oxidation-Reduction Systems in Milk." By R. T. S. Twigg, B.Sc.

"Some Recent Work on the Lipase and Phosphatase of Cow's Milk." By Professor H. D. Kay, O.B.E., Ph.D., D.Sc., E. C. V. Mattick, M.Sc., Ph.D., and S. J. Folley, M.Sc., Ph.D.

"Present Knowledge of the Minor Nitrogenous Constituents of Milk." By J. H. Bushill, D.Sc., A.I.C., L. H. Lampitt, D.Sc., F.I.C., and D. F. Filmer, B.Sc.

"The Estimation of Catalase in Milk." By E. B. Anderson, M.Sc., F.I.C., and R. MacWalter, Ph.D.

The February meeting of the Society was a Joint Meeting with the Food Group of the Society of Chemical Industry, and was devoted to a discussion on "The Less-known Constituents of Milk and their Examination."

The paper by Dr. W. R. Schoeller on "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates, XXXIII," summarises the results of a protracted research. The President congratulated Dr. Schoeller on the conclusion of this important piece of work, and the Council is pleased to be able to state that, in view of the fact that Dr. Schoeller's work has been published in its entirety in THE ANALYST, it has been decided to approve the publication of a monograph on the work under the auspices of the Society.

THE ANALYST.—Not only has THE ANALYST shown a further increase in size, the number of pages being 882, as compared with 858 in 1935, but it has also created a new record for the number of copies sold to subscribers outside the

Society. The accelerated demand for the journal made it necessary to increase the numbers printed, first to 2000 in July, 1936, and then to 2200 in January, 1937.

The outstanding feature in connection with the papers published in THE ANALYST has been the increase in the number of those relating to inorganic analysis. Of the 58 papers that appeared in Volume 61, 17 were concerned with inorganic analysis and 22 with the examination of food and drugs. The same trend is to be observed in the subject-matter of the Notes, 10 of the total of 31 relating to inorganic analysis and 10 to food and drugs. It is gratifying to have such proof that the journal is now becoming recognised by inorganic chemists as the most suitable medium for the publication of their analytical papers.

The customary extracts from the reports of Public Analysts and Government Analysts at home and abroad have been published, and the extending interest attaching to these extracts is shown by the fact that the Editor now receives similar reports from Government Departments in the United States of America and in South America.

The book reviews have continued to afford a useful guide to new publications of direct or indirect analytical importance; sixty-three books in all have been reviewed.

TREASURER'S REPORT.—The Hon. Treasurer reports that the financial position of the Society is satisfactory, income being slightly in excess of expenditure.

HONORARY MEMBERSHIP OF THE SOCIETY.—The Council is very pleased to record that Mr. B. C. Aston, F.I.C., until recently Dominion Agricultural Analyst, New Zealand, and Dr. R. H. Pickard, D.Sc., Ph.D., F.I.C., F.R.S. (President of the Institute of Chemistry), have been elected Honorary Members of the Society.

BEILBY MEMORIAL AWARD.—The Council congratulates Dr. B. S. Evans, one of the two recipients of the Sir George Beilby Memorial Award for 1936. The Award is made in recognition of continuous work of exceptional merit, bearing the evidence of distinct advance in metallurgical knowledge and practice.

The Council has also congratulated Sir Gilbert Morgan on the Honour of Knighthood (Birthday Honours, 1936) and Dr. J. J. Fox on his appointment as Government Chemist.

ANALYTICAL METHODS COMMITTEE.—Three reports from this Committee have been published during the past year, *viz.*:

"The Determination of Ascaridole in Wormseed Oil," ANALYST, 1936, **61**, 179.

"The Reichert–Polenske–Kirschner Process (as applied to Butter-fat)," ANALYST, 1936, **61**, 404.

"The Determination of Free Alkali in Soaps," ANALYST, 1937, **62**, 36.

In addition to the existing sub-committees, two new ones have been appointed: (1) under the Chairmanship of Mr. A. More, to examine the possibility of standardising the Reichert–Polenske–Kirschner process so as to give reproducible results with oils and fats generally, and (2) a Poisons Sub-Committee, under the Chairmanship of the President, to standardise methods of assay for certain substances appearing in the Poisons Schedules of the Pharmacy and Poisons Act, 1933. This Sub-Committee is examining, in the first instance, preparations of lobelia, gelsemium, aconite, and ephedra (ANALYST, 1936, **61**, 653).

The work of other sub-committees is progressing satisfactorily, and further reports are expected to be ready for publication in the near future.

ANALYTICAL INVESTIGATION SCHEME.—The series of investigations by Dr. Schoeller and his co-workers, to which reference has already been made, was carried out under the Scheme. Three other investigations are in progress.

NORTH OF ENGLAND SECTION.—The Hon. Secretary reports that five meetings have been held, at which the following papers have been read:

"The Ash of Vegetable Drugs; its Importance and Determination." By A. D. Powell, A.I.C.

"The Estimation of the Original Freezing-point of Sour Milk." By H. J. Evans, B.Sc., F.I.C.

"The Abolition of Vitamins." By A. L. Bacharach, M.A., F.I.C.

"Some Aspects of the Analysis of Meat and Bone Meals." By J. G. Sherratt, B.Sc., F.I.C.

"Sussex Ground Oats." By F. Robertson Dodd, F.I.C., and A. Pattinson Telford.

"Notes on the Addendum, 1936, to the British Pharmacopoeia, 1932." By J. R. Walmsley, F.I.C.

Discussion introduced by F. W. M. Jaffé, B.Sc., F.I.C., on: "The Possibility of Extending the Application of the Principle of Agreed Standards and Limits in Connection with Samples taken under the Food and Drugs Act."

Discussion introduced by S. E. Melling, F.I.C., on: "The Question of Changing the Name of the Parent Society."

The attendances have been quite up to the level of previous years, and the interest has been fully maintained. The April meeting was favoured with a visit by the President.

In December a ballot was taken of members of the Section on the question of changing the name of the Parent Society.

In June a very well-attended Summer Meeting was held at Blackpool, where, perhaps to a greater degree than on any previous occasion, members availed themselves of the opportunities afforded for social intercourse.

Eleven members have joined the Society through the Section.

Eighty-nine subscriptions have been received, which is an advance of thirteen on the highest previously recorded.

The thanks of the Secretary are due to Mr. Arnold R. Tankard (Chairman) and to the Committee for their constant support and for their efforts which have accomplished the successful working of the Section through the year.

SCOTTISH SECTION.—Four meetings were held in 1936, one of which was a joint meeting with the Food Group of the Society of Chemical Industry. The following seven papers were read and discussed:

"The Composition of Scottish Raspberries." By Andrew Dargie, B.Sc., A.I.C.

"The Determination of Lead in Potable Waters." By S. L. Tompsett, Ph.D., B.Sc., F.I.C.

"Some Observations on the Behaviour of Calgon in the Animal Organism." By Dr. W. O. Kermack, Dr. H. Dryerre and W. T. Spragg.

"An Improved Method for the Determination of Lactic Acid." By Dr. John P. Dickson.

"Some Notes on the Perchlorate Method for the Determination of Potash." By A. M. Cameron, B.Sc., F.I.C.

"Note on the Determination of Lead in Water." By J. W. Hawley, B.Sc., F.I.C., and W. Wilson, F.I.C.

"The Analysis of Peaty Waters." By R. T. Thomson, F.I.C.

CONGRESSES, ETC.

Royal Sanitary Institute.—The Society was represented by Messrs. E. B. Anderson and E. Hinks at a conference on:

"The Administration of the Milk (Special Designations) Order, 1936, with reference to Accredited Milk."

International Commission for the Study of Fats.—The Society was represented directly on the British Standards Institution Section of the Commission by Dr. H. E. Cox, in addition to the Chairman of the Section—Mr. E. R. Bolton.

In conclusion the Council desires to place on record its thanks to those members who have aided the work of the Society by service on its Committees and by representing the Society on various bodies.

(*Signed*) G. ROCHE LYNCH, *President.*
LEWIS EYNON, *Hon. Secretary.*

Less-known Constituents of Milk and their Examination

THE following five papers were read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry on February 3rd, 1937:

SOME MINOR COMPONENT ACIDS OF MILK-FATS AND THEIR POSSIBLE SIGNIFICANCE

BY T. P. HILDITCH, D.SC., F.I.C.

The ordinary process of ester fractionation analysis permits the approximate quantitative composition of the component acids of milk-fat to be obtained; typical figures are shown in Table I (weight percentages) and Table II (molar percentages).

TABLE I

MILK-FATS FROM PASTURE-FED COWS IN DIFFERENT LOCALITIES

Component fatty acids per cent. (weight)

	England (Berkshire)			New Zealand	India
	Autumn-fed	Early summer pasture		December pasture	Pasture-fed
Acid	1928	1929	1932	1928	1929
Butyric ..	3·1	3·3	3·1	3·5	2·6
Caproic ..	1·7	1·3	1·7	1·7	1·9
Caprylic ..	1·6	1·2	0·7	1·3	1·4
Capric	2·1	2·2	1·8	3·1	3·6
Lauric ..	3·4	4·0	3·2	4·1	5·7
Myristic ..	6·9	10·4	7·1	11·1	10·6
Palmitic ..	29·0	26·1	22·8	27·3	29·1
Stearic.. ..	7·6	6·5	12·5	11·5	6·7
Arachidic (?) ..	0·9	—	0·7	0·6	—
Oleic	40·1	40·9	41·3	31·3	34·0
Linoleic (?) ..	3·6	4·1	5·1	4·5	4·4

Owing to the wide variation in molecular weight of the component acids, it is necessary to consider the molar percentage figures in order to see in a true perspective the relative abundance of any of the acids. We see that oleic, followed closely by palmitic, is the predominating milk fatty acid. Three acids compete for the third place: butyric, myristic and stearic, each claiming 7 to 10 mols. out of every 100 mols. of total milk fatty acids; butyric acid is somewhat more constant in amount than myristic or stearic acid.

The remainder of the milk fatty acids may be considered to be *minor* components, and therefore fall within the scope of the present discussion.

TABLE II

MILK-FATS FROM PASTURE-FED COWS IN DIFFERENT LOCALITIES

Component fatty acids per cent. (molar)

	England (Berkshire)			New Zealand	India
	Autumn-fed	Early summer pasture		December pasture	Pasture-fed
Acid	1928	1929	1932	1928	1929
Butyric	8·4	8·9	8·5	9·2	6·9
Caproic	3·5	2·7	3·5	3·4	4·0
Caprylic	2·7	2·0	1·2	2·2	2·2
Capric	2·9	3·0	2·6	4·2	4·9
Lauric	4·1	4·7	3·8	4·7	6·7
Myristic	7·2	10·9	7·5	11·5	10·9
Palmitic	27·1	24·3	21·6	25·0	26·8
Stearic	6·4	5·4	10·7	9·5	5·5
Arachidic (?)	0·7	—	0·6	0·5	—
Oleic	33·9	34·6	35·6	26·1	28·4
Linoleic (?)	3·1	3·5	4·4	3·7	3·7

SATURATED ACIDS.—*Caproic-capric Acids.*—Caproic acid is usually more prominent than the other two acids, the amounts of the latter often being only of the order of 2 per cent. of the total milk fatty acids. It is, of course, known that these statements only apply to cow milk-fats. The milk-fats of other animals frequently contain much less butyric acid, while those of sheep and goats are much richer than cow milk-fat in caprylic and capric acids.

Lauric Acid.—This acid is usually included in the list of milk-fat acids, but the evidence for its presence is not altogether convincing; up to the present, no definite identification of lauric acid in the mixed acids of butter appears to have been put on record.

Saturated Acids of Higher Molecular Weight than Stearic Acid.—The small proportions present are calculated in our analyses to arachidic (C_{20}) acid, but the presence of the latter has been disputed by Bosworth and Brown.[1] Recently, Helz and Bosworth[2] qualitatively examined the higher saturated acids present in 360 lbs. of butter-fat, and stated that more than half (about 0·25 per cent. of the total fatty acids) consisted of "cerotic" (C_{26}) acid; they also observed smaller quantities of arachidic, behenic and lignoceric acids. It is reasonable to suppose that this minute proportion of "cerotic" acid is derived from the waxes of the grass eaten by the cattle.

UNSATURATED ACIDS.—Greater interest, perhaps, centres in recent work on these; this has been concerned chiefly with the identity of the octadecadienoic ("linoleic") acid, if it is present, with the occurrence of certain mono-ethenoid acids of lower molecular weight than oleic acid, and with the traces of poly-ethenoid acids of higher molecular weight than oleic acid.

Octadecadienoic Acid.—In our ester-fractionation analyses we have calculated the unsaturated C_{18} esters to a mixture of oleic and "linoleic," *i.e.* octadecadienoic esters, although we were unable (*cf.* Hilditch and Jones[3]) to account qualitatively for more than traces of ordinary linoleic acid (as evidenced by conversion to the characteristic tetrahydroxystearic acids). Bosworth and Brown[1] denied the presence of any linoleic acid in butter-fat and ascribed any excess unsaturation to arachidonic acid; but Green and the writer,[4] while admitting the presence of "arachidonic acid" in the minute amounts given by Bosworth and Brown, showed that the iodine values of the C_{18} unsaturated esters involved the presence of much greater proportions of a poly-ethenoid C_{18} acid than could thus be accounted for, that no tetra-ethenoid and almost certainly little or no tri-ethenoid acid of the C_{18} series was present, and that the C_{18}-acids of iodine value about 115 (the richest concentrate which could be prepared) yielded, on disruptive oxidation, azelaic, nonoic and hexoic acids, thus pointing conclusively to a mixture of $\Delta^{9:10}$-oleic acid and a $\Delta^{9:10,12:13}$-octadecadienoic acid. Since the octadecadienoic acid of grass glycerides also fails, to some extent, to give the usual reactions of "linoleic" acid, it seems likely that there is a connection here, and that the difference between the octadecadienoic acids of grass and milk glycerides and of seed-fat glycerides may be due to the presence of different geometrical (*cis-trans*) isomerides of the di-ethenoid acid. There, for the moment, the matter rests, so far as the writer is aware; but it cannot be claimed that the mystery of the milk-fat octadecadienoic acid has yet been disposed of completely and satisfactorily.

Lower Mono-ethenoid Acids.—Ida Smedley[5] detected, in 1912, the presence of small amounts of a decenoic acid in butter-fat; and Grün and Wirth,[6] working on the acids from 500 kilos. of butter in 1922, isolated sufficient of this acid to establish its constitution as the $\Delta^{9:10}$-decenoic acid, and also reported the presence of tetra- and hexa-decenoic acids. Bosworth and Brown[1] confirmed the observations of Grün and Wirth as to the presence of $\Delta^{9:10}$-decenoic acid and a tetradecenoic acid, and gave the approximate amounts of these as 0·2 and 0·9 per cent., respectively, of the total fatty acids; but they failed to detect any hexadecenoic acid. Riemenschneider and Ellis,[7] however, reported 2·1 per cent. of hexadecenoic acid, as well as 0·4 per cent. of tetradecenoic and 0·2 per cent. of decenoic acid, in goat milk-fat. By modifying the refractionation procedure applied to the unsaturated esters, Hilditch and Thompson,[8] and Hilditch and Paul,[9] obtained definite evidence of the presence of both tetra- and hexa-decenoic acids, and were able to make an approximate calculation, with allowance for decenoic, tetra- and hexa-decenoic acids. The results accord well in each case with Bosworth and Brown's estimate of the proportions of decenoic and tetradecenoic acids, but point to the presence of 3 to 5 per cent. of hexadecenoic acid in addition (the analysis of the saturated acids in completely hydrogenated butter-fat by Hilditch and Paul conformed with the data obtained by allowing for these minor unsaturated acids).

The data in Table III illustrate the difference in composition of the fatty acids resulting from allowance for these minor unsaturated component acids. The main difference is a drop of 5 to 6 per cent. in the oleic acid, the presence of 5 per cent.

of hexadecenoic acid, and relatively small alterations in the proportions of lauric, myristic and palmitic acids.

TABLE III

ALTERNATIVE CALCULATIONS FROM FRACTIONATION DATA

(allowing for presence of minor lower unsaturated acids)

	Weight percentages		Molar percentages	
Acid	Old calculation	Modified calculation	Old calculation	Modified calculation
Butyric	3·7	3·7	9·8	9·8
Caproic	2·0	2·0	4·1	4·1
Caprylic	1·3	1·0	2·1	1·6
Capric	2·7	2·6	3·7	3·5
Lauric (?)	4·0	1·7	4·8	2·0
Myristic	7·9	9·3	8·2	9·6
Palmitic	23·8	25·4	21·9	23·4
Stearic	10·7	10·7	8·9	8·9
as Arachidic	0·5	0·4	0·3	0·3
as Decenoic	—	0·2	—	0·3
as Tetradecenoic ..	—	1·2	—	1·3
as Hexadecenoic ..	—	5·0	—	4·6
as Oleic	38·3	32·4	31·9	27·0
as Octadecadienoic ..	4·7	4·0	4·0	3·3
as C_{20-22} unsaturated ..	0·4	0·4	0·3	0·3

The constitution of the tetra- and hexa-decenoic acids was not given by the earlier workers, but Hilditch and Paul[9] have shown that in these the ethenoid linking is also in the 9:10 position; this point is returned to later in the present paper.

Higher Poly-ethenoid Acids.—The work of J. B. Brown and his colleagues has shown that milk-fat contains traces (of the order of 0·3 to 0·4 per cent. as a rule) of highly unsaturated acids, which Brown considers to be exclusively the tetra-ethenoid arachidonic acid, $C_{20}H_{32}O_2$. In my opinion, while arachidonic acid may be the chief component, there are probably other poly-ethenoid (tetra- and penta-ene) acids present, possibly of the C_{22} as well as of the C_{20} series. The occurrence of similar minor amounts of these acids in the depot-fats of land animals has frequently been recorded, whilst in those of amphibians and reptiles their amount is increased, and, of course, the poly-ethenoid C_{20} and C_{22} acids are important major components of most fats occurring in aquatic fauna and flora (*cf.* Hilditch and Lovern[10]).

The possible significance of some of the minor unsaturated components of milk-fat in connection with the processes involved in milk-fat formation will next be considered.

A POSSIBLE MODE OF FORMATION OF THE ACIDS OF LOWER MOLECULAR WEIGHT IN MILK-FAT GLYCERIDES.—Earlier work on the glyceride structure of a wide variety of natural fats has shown that the proportion of fully-saturated glycerides in certain animal depot-fats and in milk-fats is definitely greater (for a given proportion of saturated acids in the total fatty acids) than in vegetable depot-

(seed) fats or in animal depot-fats which contain only small proportions of stearic acid. The general relationships for all types of natural fat are shown in Fig. 1.

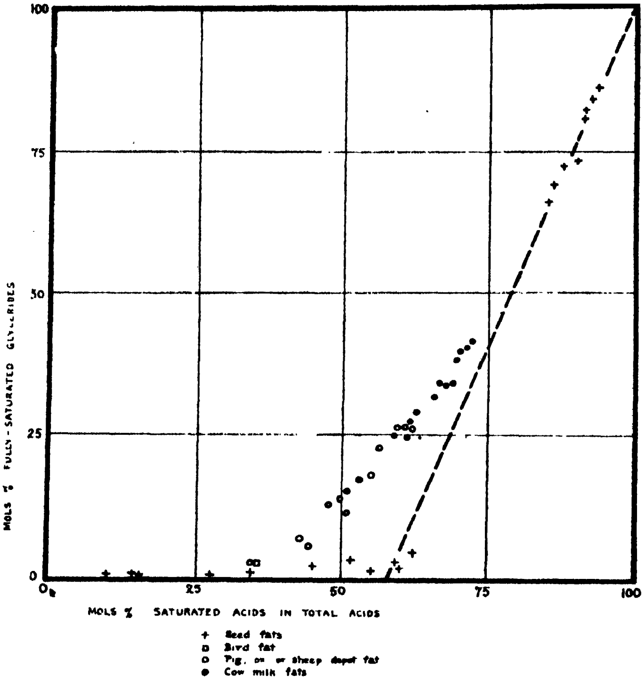

Fig. 1

Fig. 2 shows the same graph on an enlarged scale, covering the range of lards, tallows and milk-fats. The positions of the latter are near to a fairly smooth curve which intersects the horizontal axis at a point corresponding to 25 to 30 per cent. of saturated acids—the amount of palmitic acid invariably found in these fats. The abnormal increase in fully-saturated glycerides in the depot-fats runs exactly parallel with increasing amounts of stearic acid present in the glycerides. The observed relationships can, in fact, readily be explained by the hypothesis that, in these depot-fats, the increased proportions of fully-saturated glycerides are due to hydrogenation or saturation of pre-formed oleo-glycerides into stearo-glycerides. This possibility is well illustrated by the curve (Fig. 2) obtained when a pig depot-fat of low stearic acid-content was hydrogenated under laboratory conditions.

It will be seen, however, that the milk-fat relationships fall in exactly the same category as the depot-fat; indeed the two series of fats overlap on the graph, the most unsaturated butter-fats containing a smaller proportion of saturated acids than the most saturated tallows.

To apply the same hypothesis to the milk-fat glycerides involves, however, more than simple hydrogenation of oleo-glycerides; it demands the conversion of an oleo-glyceride into, for example, a butyro- or capro-glyceride, and this involves a process of combined oxidation and reduction which, moreover, must not involve the free carboxyl group, since it is the glyceride itself which must be transformed. This conception seems less unlikely at the present time than when it was first suggested by Hilditch and Sleightholme[11] in 1930. At that time it was generally held that blood phospholipins were the probable precursors of milk-fat, but subsequently, and especially in consequence of the work of Graham, Jones and Kay,[12] it has been shown that milk-fat glycerides are derived mainly from the non-phospholipin fatty acids of blood, probably from those of neutral fat (glycerides). Moreover, the former view that oxidation of fats *in vivo* was confined to the "β-oxidation" process commencing from the free carboxylic acid groups has been replaced by Jowett and Quastel's[13] conception of "multiple alternate oxidation," *i.e.* oxidation at alternate carbon atoms of a long carbon chain; while Verkade and Lee[14] have shown that, under certain conditions, oxidation of a terminal methyl group takes place in the living organism.

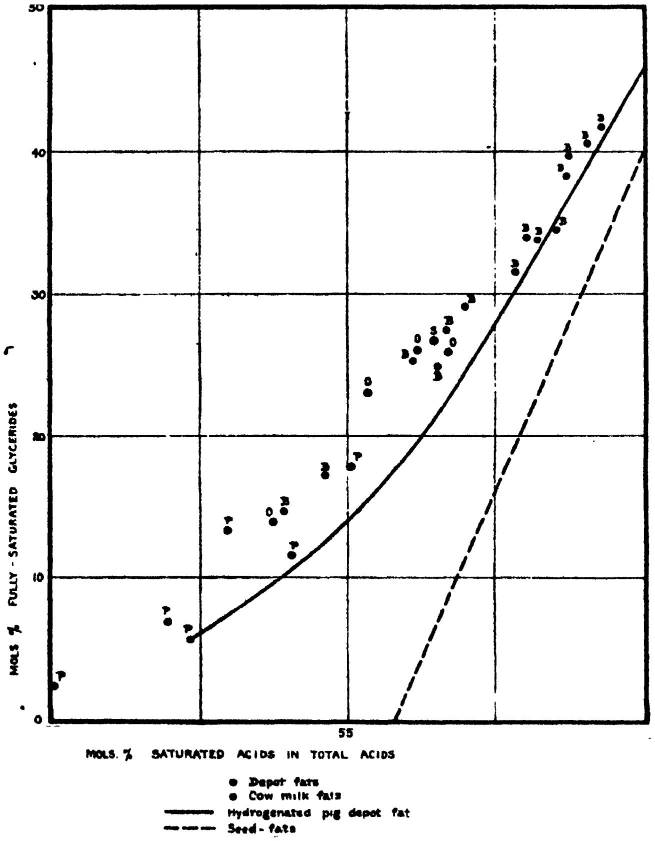

Fig. 2

Prima facie, therefore, the hypothesis that lower saturated fatty glycerides might be produced *in vivo* from pre-formed oleo-glycerides is not in fundamental conflict with the present views on the precursors of milk-fat, or on the mechanism of oxidation processes possible in a long carbon chain. Two pieces of additional evidence in favour of the views put forward may be derived from recent observations on some of the minor components of milk-fats.

The Lower Mono-ethenoid Acids.—Hilditch and Paul[9] oxidised an ester-fraction rich in tetra- and hexa-decenoate and almost, if not wholly, free from oleate, and obtained a large yield of azelaic (but no other dibasic) acid, whilst *n*-heptoic acid was identified amongst the monobasic acids. It therefore appears that the position of the ethenoid linkage in all three acids ($\Delta^{9:10}$) is the same as in oleic acid:

TABLE IV

$\Delta^{9:10}$-Decenoic acid	$CH_2:CH.[CH_2]_7.CO_2H$
$\Delta^{9:10}$-Tetradecenoic acid	$CH_3.[CH_2]_3.CH:CH.[CH_2]_7.CO_2H$
$\Delta^{9:10}$-Hexadecenoic acid	$CH_3.[CH_2]_5.CH:CH.[CH_2]_7.CO_2H$
Oleic acid	$CH_3.[CH_2]_7.CH:CH.[CH_2]_7.CO_2H$

This circumstance, together with the absence of any unsaturated acid lower in the series than decenoic acid (which was also proved analytically), suggests that these minor components of milk-fat may represent fragments, so to speak, of transformed oleo-glycerides which have escaped complete saturation to lower saturated glycerides.

EFFECT OF INGESTED COD-LIVER OIL ON MILK-FAT.—When cod-liver oil is included in the diet of cows there is, in addition to a lowered production of milk-fat, a very marked alteration in its composition (Table V). The lower saturated fatty acids are reduced to about half their usual proportion, the myristic and stearic acid contents are also reduced, but to a less extent, while the oleic acid content is considerably increased, and several per cent. of the highly unsaturated C_{20} and C_{22} acids, characteristic of cod-liver oil, appear instead of the usual fractional percentage of "arachidonic" acid.

TABLE V

COMPONENT ACIDS OF MILK-FATS FROM A COW RECEIVING COD-LIVER OIL (weight per cent.)

Acid	Normal diet	With cod-liver oil
Butyric	4·4	2·1
Caproic	1·8	0·9
Caprylic	2·1	0·5
Capric	2·8	1·2
Lauric	3·8	3·1
Myristic	10·1	6·4
Palmitic	25·3	22·7
Stearic	12·4	6·7
as Arachidic	0·8	0·6
as Oleic	31·0	43·3
as Octadecadienoic	4·4	4·8
as C_{20-22} unsaturated	1·1	7·7

When linseed oil or rape oil is similarly fed, the corresponding milk-fats are unaffected as regards the proportions of lower saturated acids present, the only significant alteration being an increased oleic acid content balanced by somewhat less palmitic and/or myristic and stearic acids. A little of the C_{22} mono-ethenoid erucic acid of rape oil appears in the milk-fat, but on a linseed oil diet the characteristic linolenic and linoleic acids of this oil do not appear in detectable amounts in the milk-fat.

The highly unsaturated C_{20} and C_{22} acids of cod-liver oil, however, evidently pass into the milk glands to quite an appreciable extent. The effect on the yield and composition of the milk-fat is of a temporary nature, *i.e.* the milk-fat returns to normal within a few days after the cod-liver oil diet is stopped. The effect is consistent with a temporary interference with the enzymes concerned in milk-fat elaboration; if the formation of the lower fatty glycerides of butter is due to enzymic oxidation-reduction of oleo-glycerides, highly unsaturated glycerides of the cod-liver oil will undoubtedly be preferentially adsorbed by the enzymes concerned, which would therefore be partially "poisoned" or hindered from carrying out their normal functions.

If, instead of comparing the percentage compositions of the butter fatty acids, we use these (in conjunction with the weights of butter-fat produced per day) to obtain a rough measure of the weight of each component acid produced daily as butter glycerides (Table VI), the effect on the total yield of milk-fat is seen, together with the following points concerning individual acids: butyric and caproic acid production is reduced to one-third of the normal; that of butyric-lauric (taken together) is similarly reduced; myristic and stearic production is reduced by over 50 per cent., palmitic by about one-third, while the amount of oleo-glycerides produced is unaffected or very slightly reduced. In other words, the glycerides which suffer most in production are precisely those which, on the hypothesis suggested, are produced by oxidation-reduction processes from oleo-glycerides.

TABLE VI

APPROXIMATE WEIGHT PRODUCTION OF MILK FATTY ACIDS IN A COW RECEIVING 4 OZS. DAILY OF COD-LIVER OIL IN FOOD

	Before lb.	During lb.	Immediately after lb.	After 2 weeks lb.
Milk-fat production per day	7·91	5·60	5·33	7·76
Corresponding butter fatty acids	7·51	5·33	5·07	7·37
Butyric acid	0·33	0·11	0·11	0·33
Caproic „	0·13	0·05	0·05	0·13
Caprylic „	0·16	0·03	0·03	0·16
Capric „	0·22	0·06	0·06	0·22
Lauric „	0·28	0·16	0·16	0·27
Myristic „	0·76	0·34	0·32	0·75
Palmitic „	1·90	1·21	1·15	1·86
Stearic „	0·93	0·36	0·34	0·91
Arachidic „	0·06	0·03	0·03	0·06
Oleic „	2·33	2·31	2·19	2·28
Octadecadienoic acid ..	0·33	0·26	0·24	0·32
C_{20-22} unsaturated acids ..	0·08	0·41	0·39	0·08

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DISCUSSION

Professor H. D. KAY said that there was one point to which he would venture to draw attention. It appeared, from other work, that at low and medium temperatures (of the physiological range) relatively unsaturated fats were more readily formed and transported in the living organism than relatively saturated fats. Possibly some of the differences in saturation between depot and milk fats reported by Professor Hilditch might be associated with temperature differences or with transport difficulties.

Captain J. GOLDING said he was glad that Professor Hilditch had mentioned the experiments at Reading in which cows had been fed with 4 to 8 oz. of cod-liver oil daily. Not only was the composition of the fat in the milk of such cows altered, but the percentage of fat in the milk was reduced by half.

Mr. A. L. BACHARACH said that one point of interest in Professor Hilditch's "speculative" views of fatty acid degradation was that it did not involve, as did any theory based on β-oxidation, hydrolysis of glycerides followed by reglycerification.

Dr. H. E. COX remarked that one gathered from general reading on this subject that milk-bearing animals took the path of least resistance in fatty synthesis. If they could get the fatty acids or glycerides directly from their food they did so, if not they synthesised them from other material. Professor Hilditch referred to cerotic acid in grass; there was little, if any, of this acid in milk-fat; so that it must be split up in the cow. If that were so and a C_{18} acid was produced from the C_{26} acid, was there any evidence of lower fatty acids with 8 or less carbon atoms arising from the splitting of the C_{26} acids?

Professor HILDITCH, replying, said that the question of temperature might well play a part. He thanked Captain Golding for reminding him of two points he had omitted in his rather hurried review of this work. He had forgotten to mention the small amount of cod-liver oil that would produce the effect, namely, 4 ozs. a day; also, that the effect was quite temporary. It was stressed that not only was the quantity of the fat affected, but also its composition was entirely altered.

Regarding Dr. Cox's query, he was afraid that there had been a little misunderstanding. Evidently he had not made it quite clear that, in the case of cerotic acid, only a little got through; he did not suggest that the rest was used: it was probably excreted. He was not suggesting that this acid was broken down. He had rather a strong feeling that the primary acid found in natural fats was, very largely, oleic acid, or, more probably, oleic glycerides.

SOME RECENT WORK ON THE LIPASE AND PHOSPHATASE OF COW'S MILK

By H. D. Kay, O.B.E., Ph.D., D.Sc., E. C. V. Mattick, M.Sc., Ph.D., and S. J. Folley, M.Sc., Ph.D.

(*Abstract*)*

After outlining the methods of estimating phosphatase the authors described the difficulties of devising a satisfactory method of estimating lipase in milk. The best results were ultimately obtained by the use of tributyrin in association with a special buffer, at pH 8·5, and with bacteriological control before and after the estimation, the hydrolysed butyric acid being distilled off and titrated. The conditions as to shaking, etc., must be rigidly standardised.

It was shown that all raw milks contain lipase in amounts varying from cow to cow and during the lactation period. Milk lipase is more readily destroyed by heat than is phosphatase. There is more lipase in milk serum than in milk-fat, but the reverse applies to phosphatase. It is probable that the lipase and phosphatase in milk are unrelated, and that the phosphatase-content affords an index of the efficiency of the mammary gland.

THE ESTIMATION OF CATALASE

By E. B. Anderson, M.Sc., F.I.C., and R. J. McWalter, Ph.D.

(*Abstract*)*

In continuation of work on the enzymes of milk it became necessary to study the methods proposed for the estimation of catalase. These fall into two main groups, distinguished by gas volumetric measurement of the oxygen evolved from hydrogen peroxide, and volumetric estimation of the peroxide undecomposed, either directly with potassium permanganate or indirectly by iodine liberation from potassium iodide. These tests are critically surveyed and a modified iodimetric test is described which avoids the difficulties experienced by other

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* The paper will be published in the *Journal of the Society of Chemical Industry*, 1937.

workers. It is pointed out that the estimation cannot be other than on an empirical basis, as the substrate gradually destroys the enzyme, and therefore conditions have been chosen which allow the reaction to approach completion in a reasonable time with maximum destruction of substrate. The results agree quite well with those obtained by a refined gasometric method.

PRESENT KNOWLEDGE OF THE MINOR NITROGENOUS CONSTITUENTS OF MILK

By J. H. Bushill, D.Sc., A.I.C., L. H. Lampitt, D.Sc., F.I.C.,
and D. F. Filmer, B.Sc.

(*Abstract*)*

Casein, albumin and globulin constitute about 93 per cent. of the nitrogenous constituents of milk, and the remainder (including amino acids and amides, phosphatides, purine substances, ammonia, choline, thiocyanate and lactoflavine) are to be regarded as the minor constituents. The trichloroacetic acid precipitation method has given the most satisfactory results for the precipitation of the proteins. For ammonia, steam-distillation under reduced pressure has given good results, for urea a modification of the urease method has been devised, and for creatinine a modification of the colorimetric method with picric acid has been used to eliminate the influence of lactose.

OXIDATION-REDUCTION SYSTEMS IN MILK

By R. S. Twigg, B.Sc.

(*Abstract*)*

Investigations were carried out to ascertain the capacity of raw and heated milks (whole and skimmed) to reduce a standard concentration of methylene blue, apart from the reducing activities of any bacteria. The work was of importance in view of the recent introduction of the methylene blue test for the bacteriological grading of milk under the Milk (Special Designations) Order, 1936. A special milk was used, of very low bacterial count, and no multiplication of the bacteria occurred during the progress of the investigations, which were carried out in the absence of oxygen.

From the results obtained it was thought justifiable to consider that raw milk possesses a natural reducing system of its own. Skim milk does not reduce methylene blue, separation of the cream removing reducing substances and any enzymes necessary to reduction. Heating to 63° C. for half-an-hour, *i.e.* pasteurisation, wholly or partially inhibited enzymes necessary for the full activity of the reducing system of whole milk. Pasteurised skim milk behaved like pasteurised whole milk, but with even less reducing activity. Cream, itself,

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* The paper will be published in the *Journal of the Society of Chemical Industry*, 1937.

if left unheated and suspended in water, reduced methylene blue. Pasteurisation, or heating to a higher temperature, destroyed its reducing activity.

Many substrates were tested for their ability to reduce methylene blue in the presence of washed cream or membrane suspensions. Of all these, only aldehydes and hypoxanthine showed definite reducing activity. Attempts were made to dialyse either whole milk or unwashed cream with a view to building up the reducing system. No success had been attained, and it appeared that dialysis rather quickly inactivates certain of the enzymes. Recent experiments showed that the ascorbic acid-content of milk played little or no part in the reduction of methylene blue under anaerobic conditions.

A Rapid Method for the Determination of Triethanolamine

BY C. J. EASTLAND, F.I.C., NORMAN EVERS, B.Sc., F.I.C.,
AND T. F. WEST, B.Sc., A.I.C.

(*Read at the Meeting, December* 2, 1936)

IN view of the increasing number of products containing triethanolamine as a constituent, a rapid method for its determination, especially in the presence of large quantities of non-saponifiable substances, is very desirable. Fleck[1] has already described a method in which the saponified material is evaporated to dryness with lime and the triethanolamine extracted with boiling alcohol. This method has been found unsatisfactory when applied to many preparations, *e.g.* toilet creams containing a high proportion of unsaponifiable matter, because not only is the extraction of the triethanolamine from the complicated mixture after saponification not always complete, but the base is frequently contaminated with substances not readily removed in subsequent treatment. We have therefore carried out experiments involving extraction of the triethanolamine by means of acid, without initial saponification of the cream. Prior to the publication of the paper by Fleck, Jaffe[2] had published a method in which the triethanolamine is extracted with hydrochloric acid and determined colorimetrically. This is not always practicable, and we have devised a method whereby the triethanolamine can be obtained in a pure state (except for non-interfering substances such as glycol and glycerol) from emulsions and similar preparations, and, as it has been applied with successful results to widely different types of creams, it is suitable for the analyst investigating a product of unknown composition.

PREPARATION AND DETERMINATION OF PURE TRIETHANOLAMINE.—Since commercial triethanolamine may contain 20 or more per cent. of the mono- and diethanol compounds, it was decided to prepare a sample of pure triethanolamine through the hydrochloride by the method of Germann and Knight.* The ease with which the hydrochloride could be obtained and the sharpness of its melting-point led to the method of identification and determination described in this paper.

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* The melting-point of our compound was 177° C. (Germann and Knight,[3] 177–8° C.; Knorr,[4] 177° C.; B.P.C., 173–4° C.).

Commercial triethanolamine is neutralised to methyl orange with conc. hydrochloric acid at 10 to 15° C. After standing for an hour the crystals of triethanolamine hydrochloride are filtered off, washed with 95 per cent. ethyl alcohol and dried for one hour at 110° C.*

The white solid is added to isopropyl alcohol (100 g. to 400 ml.) to which an equivalent quantity of powdered sodium hydroxide has been added. This mixture is refluxed for three hours and, after standing overnight, the precipitated sodium chloride is filtered off. The isopropyl alcohol is distilled off at atmospheric pressure, after which the triethanolamine itself distils over at 194 to 195° C. at 10 mm. pressure.

A solution of the crystals in water yielded with Kraut's reagent† the red crystalline precipitate described by Shupe[5] as characteristic for triethanolamine.

The chlorine-content has been shown by Germann and Knight to agree with the formula $N(CH_2CH_2OH)_3.HCl$.

Determination of Pure Triethanolamine.—About 0·2 g. of triethanolamine was dissolved in 2 ml. of hydrochloric acid (sp.gr. 1·16), and the solution was evaporated to dryness, when the hydrochloride formed a hard skin on the bottom of the beaker. This was dried in the steam-oven for half-an-hour and allowed to cool in a desiccator. The crystals were then washed on to a sintered glass crucible (I.G. 3) with four quantities of 5 ml. each of pure isopropyl alcohol, and dried at 100° C. to constant weight.‡ As the solubility of the unrecrystallised hydrochloride in isopropyl alcohol at 20° C. was 0·15 g. per litre, a correction of 0·003 g. was added to the weight obtained.

As will be seen from the typical results recorded in Table I, the method gave consistent results both for the purified triethanolamine and for a commercial sample.

TABLE I

	Taken g.	Found g.	Average per cent.
Triethanolamine (prepared from hydrochloride)	0·2025	0·1964	97·00
	0·2025	0·1964	
	0·2058	0·1996	
	0·2317	0·2248	
Triethanolamine (commercial)	0·2303	0·1630	71·62
	0·2303	0·1656	
	0·2303	0·1662	

The triethanolamine in the purified sample was 99·0 per cent., as calculated from its nitrogen-content.

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* After filtering off the triethanolamine hydrochloride the filtrate was evaporated with excess of barium carbonate, and the mixture of mono- and diethanolamines was recovered by boiling the mass with ethyl alcohol.

† Dissolve 8 g. of bismuth nitrate in 20 ml. of nitric acid (sp.gr. 1·18). Dissolve 27·2 g. of potassium iodide in a little water. Mix the solutions and dilute to 100 ml. (*J. Assoc. Off. Agric. Chem.*, 1930, 13, 47).

‡ Factor for $\frac{\text{Triethanolamine}}{\text{Triethanolamine hydrochloride}} = 0{\cdot}803$

The method was applied to the mixture of mono- and diethanolamines obtained during the preparation of pure triethanolamine. When 0·1 g. was taken only an oil remained in the beaker after evaporating off the hydrochloric acid and this was soluble in the isopropyl alcohol.

DETERMINATION IN THE PRESENCE OF GLYCEROL AND ETHYLENE GLYCOL.—The results given in Table II were obtained:

TABLE II

	Triethanolamine	
Glycerin added g.	added g.	found g.
0·25	0·1996	0·1959
0·97	0·1996	0·1951
1·05	0·1337	0·1293
1·19	0·1996	0·1925
Ethylene glycol added g.		
1·00	0·1996	0·1970
1·19	0·2051	0·1982
1·28	0·2247	0·2173
2·20	0·1996	0·1978

When the proportion of the polyhydric alcohol was relatively great it was an advantage to leave the hydrochloride residue for two hours in the steam-oven before treating it with the isopropyl alcohol.

EXTRACTION OF TRIETHANOLAMINE FROM EMULSIONS.—Mix about 5 g. of the cream with 20 ml. of water and heat on a water-bath for five minutes. Add sulphuric acid until a blue colour is given with Congo-red paper (about *p*H 3), and continue heating on the water-bath for another minute, adding more sulphuric acid, if required. Transfer the cooled mixture to a separator, and extract the fat with two quantities of 25 ml. of ether. Shake the ethereal extracts with 20 ml. of approximately 0·1 *N* sulphuric acid, and distil off the ether so that the ether-soluble matter is left floating in the acid.* Re-extract this with ether and add the aqueous layer to that obtained from the previous extraction. Remove the ether from the acid extract by heating on a water-bath, and precipitate the sulphuric acid by adding barium hydroxide solution. Any remaining haze due to incomplete extraction of the fatty matter is removed with the precipitate of barium sulphate. Warm the mixture, centrifuge, pour off the liquid from the sediment, and wash it with a little water. Precipitate the excess of barium by passing carbon dioxide into the boiling solution. Cool, filter and concentrate under reduced pressure to about 3 ml. Wash into a 50-ml. beaker with 15 ml. of ethyl alcohol, removing any insoluble material by filtering through a Hirsch funnel. Remove the alcohol by evaporation and add to the residue 2 ml. of hydrochloric acid (sp.gr. 1·16). Evaporate off the acid, collect and determine the triethanolamine as described above.

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* This procedure may seem unnecessary, but experience showed that low results were obtained in some cases unless this method was used.

The results obtained with various emulsions containing triethanolamine, given in Table III, are shown in Table IV.

TABLE III

EMULSIONS PREPARED CONTAINING TRIETHANOLAMINE

	I	II	III	IV	V	VI
Stearic acid	7	23	20	20	10	10
Liquid paraffin	5	–	–	–	–	–
Arachis oil	20	–	–	–	–	–
Soft paraffin	–	6	10	–	–	–
Borax	–	0·5	–	–	–	–
Glycerin	–	–	2	8	–	–
Lanoline	–	–	–	3	–	–
Sulphonated lauryl alcohol ..	–	–	–	1	–	–
Scarlet red	–	–	–	0·02	–	–
Triethanolamine (purified) ..	2	–	1	–	–	–
Triethanolamine (commercial) ..	–	1·9	–	1	2	2
Ammonium oleate	–	–	–	–	5	–
Quinine bisulphate	–	–	–	–	–	2
Paraffin wax	–	–	–	–	5	5
Water	to 100	to 100	to 100	to 100	to 100	to 100

TABLE IV

ANALYSIS OF EMULSIONS IN TABLE III

	Triethanolamine			
Emulsion No.	Added per cent.	Calculated from hydrochloride per cent.		M.p. of hydrochloride °C.
I	1·94	(a) 1·87	Mean 1·91	(a) 177
		(b) 1·97		(b) 177
		(c) 1·88		(c) 177
		(d) 1·91		(d) 177
II	1·35	(a) 1·25	Mean 1·31	(a) 176
		(b) 1·37		(b) 177
III	0·97	(a) 0·96	Mean 0·95	(a) 176
		(b) 0·94		(b) 177
IV	0·71	(a) 0·61	Mean 0·63	(a) 174–5
		(b) 0·65		(b) 174–6
		(c) 0·63		(c) 172–4
V	1·43	(a) 1·21	Mean 1·22	(a) 176
		(b) 1·23		(b) 176
VI	1·43	(a) 1·49	Mean 1·44	(a) 175–6
		(b) 1·38		(b) 176
		(c) 1·44		(c) 173–4

APPLICATION OF THE METHOD OF EXTRACTION IN THE PRESENCE OF GLYCEROL, ETC.—(a) *Glycerol.*—The results from emulsions (III) and (IV) containing glycerol were satisfactory.

(*b*) *"Sulphonated" Alcohols.*—When an emulsion contains a "sulphonated" fatty alcohol, the method of extraction is made more difficult, owing to the fact that ether-water emulsions are readily formed. A separation into two layers is usually effected if the emulsion is allowed to stand overnight, and the process may be hastened by centrifuging. On applying the method to cream IV (Table III) the crystals of triethanolamine hydrochloride separated on adding isopropyl alcohol to the viscous mixture obtained after evaporating off the hydrochloric acid and drying in the usual way. By determining the nitrogen in the commercial triethanolamine and in the oil extracted from the cream it was possible to calculate the triethanolamine (commercial) extracted. The result (0·93 per cent. of commercial triethanolamine equivalent to 0·67 per cent. of pure triethanolamine) was concordant with the determination by weighing the hydrochloride (0·63 per cent. of pure triethanolamine).

(*c*) *Ammonium Compounds.*—It is unlikely that ammonium salts would be included in a formula with the triethanolamine. In any case the evolution of ammonia after adding barium hydroxide in the process of extraction of the triethanolamine would indicate the presence of an ammonium salt, and the ammonia could be removed by boiling the solution. An emulsion was prepared (V) containing an ammonium soap and the method of extraction modified slightly in that the solution was boiled for some minutes after adding the barium hydroxide solution. The results obtained were satisfactory.

(*d*) *Alkaloids.*—An emulsion containing an alkaloid in addition to triethanolamine was prepared (VI). During the concentration of the aqueous solution obtained after filtering off the barium carbonate precipitated by carbon dioxide, a white scum was deposited on the sides of the flask. This precipitate was soluble in ethyl alcohol and gave a strong reaction with Mayer's reagent. The aqueous solution was therefore concentrated to 20 ml., cooled, and filtered into a clean flask, the precipitate being washed with 5 ml. of cold water. The evaporation was then continued under reduced pressure to approximately 3 ml., the solution of triethanolamine was washed into a beaker with 15 ml. of ethyl alcohol, and the triethanolamine was determined as in the general method. It is an advantage that the presence of an alkaloid would be indicated in an unknown sample. The melting-point of the hydrochloride of the base extracted is recorded in the table, and a solution in water yielded only a faint reaction with Mayer's reagent.

(*e*) *Various other Materials.*—Titanium dioxide and modern proprietary emulsifiers, including modified fats and cellulose derivatives, did not interfere, and themselves gave negative results.

NOTE ON MIDDLETON'S TEST FOR ETHYLENE GLYCOL.—Consideration of the formula of triethanolamine indicated the possibility of hydrolysis taking place during the extraction, with the formation of ethylene glycol. The following experiment was carried out to settle this point:—A commercial sample of triethanolamine was boiled for a prolonged period with 10 per cent. sulphuric acid, barium carbonate was added in excess, the mixture was evaporated to dryness and the triethanolamine was recovered by boiling the mass with alcohol. It was then found that a positive reaction could be obtained for ethylene glycol by the qualitative test described by Middleton.[6] This method involves evaporation with nitric acid, and when untreated triethanolamine was subjected to the process, a positive reaction for ethylene glycol was again obtained. This seemed to show that hydrolysis into ethylene glycol could take place under the conditions of Middleton's test, but, as it did not appear to occur during the determination as hydriodide (Fleck, *loc. cit.*) or hydrochloride, the matter was not considered further. However, the fact that a positive test was obtained, means that in applying Middleton's test for ethylene glycol, triethanolamine must first be removed. Experiments were therefore carried out to test the possibility of precipitating the base in order to free it from any water-soluble substances, particularly ethylene glycol.

SEPARATION OF TRIETHANOLAMINE FROM ETHYLENE GLYCOL BY MEANS OF PHOSPHOTUNGSTIC ACID.—Preliminary experiments showed that the most suitable reagent for this purpose was a solution of phosphotungstic acid in 5 per cent. sulphuric acid. The conditions for quantitative precipitation of the base were investigated and then applied to mixtures of ethylene glycol and triethanolamine as follows:—Mixtures of varying quantities of ethylene glycol and triethanolamine were treated with 8 ml. of water, 2 ml. of 50 per cent. sulphuric acid and 5 ml. of a 30 per cent. solution of phosphotungstic acid, and allowed to stand in the refrigerator for three days. The precipitated phosphotungstate was filtered off, the filtrate was evaporated to a small bulk with an excess of barium carbonate, and the mass was extracted with ethyl alcohol. The oil obtained after evaporating off the solvent was tested for ethylene glycol and nitrogen. In every instance the glycol had been recovered free from the base.

SUMMARY.—(1) Triethanolamine can be identified and determined as the hydrochloride.

(2) A method is described whereby triethanolamine is isolated from the water-soluble substances of emulsions and similar preparations, after acidification, advantage being taken of the insolubility of triethanolamine hydrochloride in isopropyl alcohol.

(3) Triethanolamine interferes with Middleton's test for ethylene glycol, but the base can be precipitated by phosphotungstic acid from a mixture of the two compounds, and the ethylene glycol obtained from the filtrate by the method described.

We wish to acknowledge the assistance of Mr. A. G. Jones, B.Sc., A.I.C., in carrying out a number of the analyses recorded.

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The Determination of Sulphites in the presence of Nitrates and Nitrites

By J. G. SHERRATT, B.Sc., F.I.C.

In a recent investigation it became necessary to test certain "meat pickles," consisting of meat juices in association with brine, potassium nitrate and potassium nitrite, for sulphites, and to study the rate of disappearance of added sulphur dioxide.

When samples to which sulphites had been added experimentally were tested by the well-known Monier-Williams process, no sulphur dioxide could be recovered; but the neutralised hydrogen peroxide was made acid by volatilised nitric oxides. Failure to recover sulphur dioxide in these circumstances might indicate that sulphites no longer existed in the solution tested, or, alternatively, it might be that the oxidising action of nitrates and nitrites, in the presence of the hot dilute acid necessary to the process, had destroyed sulphites during the actual analysis. In view of the evidence of the formation of volatile nitric oxides, the latter alternative appeared to be probable, and was confirmed by adding small amounts (0·1 to 0·05 g.) of potassium nitrate and nitrite to the acid liquid in the distillation flask and then running in standardised sulphite solution while the liquid boiled in a current of carbon dioxide. Under these conditions, only 10 to 15 per cent. of the weight of sulphur dioxide actually added could be recovered, and attempts to avoid the interference, by the introduction of glycerol as an "anti-oxidant" and of urea to destroy nitrites, did not improve the yield. Before the investigation could proceed, therefore, it was necessary to find a method of analysis whereby the interference of oxidising substances could be overcome.

A method for the determination of sulphites in the presence of nitrites, salt mixtures and meat products is described by Szabo.[1] This method depends upon the separation of the sulphite by precipitation as lead sulphite, followed by filtration, liberation of sulphur dioxide, and distillation into iodine solution. A trial of this method was made, but the results of test analyses carried out according to Szabo's directions were very poor with solutions of pure salts, and the method was quite unworkable in the presence of meat juices, owing to the impossibility of filtering off the precipitated protein.

After a review of the problem, it was considered that reduction of the interfering nitrate and nitrite prior to distillation of sulphur dioxide offered possibilities, but difficulty was experienced in finding an agent that would exert a selective action upon nitrate and nitrite, while leaving sulphites unattacked. A large number of reducing agents, including magnesium, aluminium, Devarda's alloy, stannous chloride and titanous chloride, were tried with various modifications of technique, but without success. These substances, for the most part, either gave appreciable "blanks" (*e.g.* Devarda's alloy) when tested with meat juices, or reduced part or the whole of the sulphur dioxide to sulphur and hydrogen sulphide. Attempts to overcome this last difficulty by preliminary conversion of the sulphite into insoluble barium sulphite did not have the effect desired. Finally, the problem was solved by the use of hydrazine sulphate in alkaline solution. The technique adopted is as follows:—

Five g. of hydrazine sulphate are dissolved in 100 ml. of hot distilled water and transferred to a flask fitted with a tap-funnel, reflux condenser and delivery tube, the arrangement of apparatus being as commonly employed in the Monier-Williams process for the determination of sulphur dioxide in foods.[3] The liquid is boiled to expel air, and cooled in a current of carbon dioxide. Twenty ml. of a 20 per cent. solution of caustic soda are added through the tap-funnel, and the flask is thoroughly shaken. The caustic soda is followed by a suitable quantity of the liquid (or, suspension of solid) to be tested, and the contents of the flask are boiled in a current of carbon dioxide for five minutes. The flame is then removed from the flask, and 10 ml. of phosphoric acid (sp.gr. 1·75), and a small quantity of pumice powder are added through the tap-funnel. The contents of the flask are boiled in a current of carbon dioxide, and the sulphur dioxide is distilled and collected in hydrogen peroxide, in the usual way. In applying this process to brine and meat pickles, it is desirable to dilute the reduced solution with boiled distilled water before the addition of phosphoric acid.

PURE SALTS.—Under these conditions meat products known to be free from sulphites gave no trace of sulphur dioxide. The method was applied to solutions of pure salts. In the first tests a known quantity of sulphur dioxide (in the form of potassium metabisulphite) was added to a solution containing 0·1 g. of potassium nitrite and 0·1 g. of potassium nitrate, the resulting mixture being treated as described. It was found that recovery of sulphur dioxide was much better than in any of the methods hitherto tried, but was not complete; the proportion recovered varied between 50 and 80 per cent. of the amount that had been added. Ultimately the loss was traced to oxidation of the sulphite before the actual analysis had started. When the sulphite solution and the nitrate-nitrite mixture were kept apart, and added to the alkaline hydrazine sulphate simultaneously through separate tap funnels, the sulphur dioxide recovered was almost equal to the theoretical amount. Some of the results obtained are given below:

Series A. (Solutions of pure salts.)

The nitrate-nitrite mixture contained 1 g. of each of the potassium salts in 100 ml.

(*a*) Direct determination of sulphur dioxide by the Monier-Williams process. Sulphite solution added to 10 ml. of nitrate-nitrite.

Sulphur dioxide added g.	Sulphur dioxide recovered g.
0·0467	0·0045

(*b*) Process as in (*a*), but solution of sulphite and 5 ml. of nitrate-nitrite introduced separately into the distillation flask.

Sulphur dioxide added g.	Sulphur dioxide recovered g.
0·0438	0·016

2. Reduction of oxidising substances with alkaline hydrazine sulphate prior to distillation of sulphur dioxide.

(*a*) Solution of sulphite mixed with 5 ml. of nitrate-nitrite solution, and the mixture added to alkaline hydrazine sulphate.

Sulphur dioxide added g.	Sulphur dioxide recovered g.
0·0457	0·0349

(*b*) Solution of sulphite and 5 ml. of nitrate-nitrite solution simultaneously added to alkaline hydrazine sulphate.

Sulphur dioxide added g.	Sulphur dioxide recovered g.
0·0219	0·0206
0·0420	0·0390
0·0429	0·0400
0·0685	0·0650

MEAT PICKLES.—The method was then applied to the determination of sulphur dioxide in commercial pickles.

Series B. Meat pickles (from commercial sources) containing brine, meat juices, nitrites and nitrates.

1. Solution of sulphite and 100 ml. pickle added separately to dilute air-free acid, and distilled (Monier-Williams process).

Sulphur dioxide added g.	Sulphur dioxide recovered g.
0·0883	0·008
0·0250	0·005
0·0438	Nil

2. Solution of sulphite and 100 ml. of pickle added separately to alkaline hydrazine sulphate.

Sulphur dioxide added g.	Sulphur dioxide recovered g.
0·088	0·076
0·044	0·036
0·072	0·063

A consideration of the above results suggests that interference with the determination of sulphur dioxide, which may be caused by nitrates and nitrites, may be overcome by the hydrazine sulphate reduction method described. Recovery of added sulphur dioxide is not entirely complete, but is probably sufficiently accurate for most practical purposes, and such small losses as occur are, perhaps, inevitable when dealing with so unstable a substance as sulphurous acid. Possibly the "neutralisation effect" described by Monier-Williams[2] may account for some of the loss noted.

With meat pickles the loss of sulphur dioxide is considerably greater than with solutions of pure salts. It is suggested that this may be due not to any defect in the process, but to factors inherent in the nature of the material. It is known that when sulphur dioxide in the form of sulphites is added to meat products, there is always an immediate loss,[3] and that amounts of sulphites added can never be recovered quantitatively. To a small extent the loss may be the result of oxidation of sulphurous acid by air entrained in the meat, but it seems probable that sulphur compounds and sulphides also play a part on the lines of the reaction:

$$2H_2S + H_2SO_3 = 3S + 3H_2O.$$

Some reaction such as this may account for the loss of sulphur dioxide from meat pickles, because, in subsequent work, it was noted that the loss assumed greater proportions when decomposing pickles were examined.

BACON AND HAM.—The investigation of the influence of nitrate and nitrite on the determination of sulphur dioxide was extended to include an examination of a few samples of ham and bacon, since, in the published account of his process, Monier-Williams[2] does not specifically mention tests of this class of foods. The amounts of nitrate and nitrite in cured meats are very variable,[4] being dependent upon the method of curing adopted, and it follows that results of tests made upon a few random samples cannot be regarded as necessarily applicable to all members of the class. With this reservation, it may be stated that, in samples of ham and bacon, there does not appear to be serious interference with the determination of sulphur dioxide by direct distillation from an acid solution. It is true that the results given below show a slightly greater recovery of experimentally added sulphur dioxide if hydrazine sulphate reduction is applied to the meat before distillation, but the extra amount recovered is small in proportion, and, as a rule, would hardly justify the additional work involved. When examining cured meats by the Monier-Williams process, however, it is probably desirable to determine sulphur dioxide gravimetrically as barium sulphate after the distillation into hydrogen peroxide, since acidity produced in the collecting liquid might be partly derived from sources other than sulphur dioxide.

Determination of Sulphur Dioxide in Samples of Bacon and Ham.—In the tests, a known volume of a standardised solution of potassium metabisulphite was thoroughly mixed with 100 g. of the minced meat, and the whole of the mixture was examined.

		Sulphur dioxide added p.p.m.	Monier-Williams process. Sulphur dioxide recovered p.p.m.	Hydrazine sulphate reduction prior to acidification and distillation. Sulphur dioxide recovered p.p.m.
No. 1.	Ham ..	540	470	495
No. 2.	Bacon ..	110	31	57
No. 3.	Bacon ..	255	130	150

			Monier-Williams process	
			Tested immediately p.p.m.	Tested after 24 hours p.p.m.
No. 4.	Bacon ..	587	490	374
No. 5.	Bacon ..	620	500	310

This paper is primarily concerned with an account of analytical work, but it may be stated that the investigation for which the work formed a necessary preliminary indicated that, when comparatively large amounts of sulphite (say 1000 p.p.m. as SO_2) are added to certain commercial meat pickles, a proportion of sulphur dioxide is still detectable after 24 hours, although the bulk of the sulphite disappears very rapidly.

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46 LEGH STREET
WARRINGTON

A New Series of Buffer Mixtures Covering the *p*H Range 1-6

BY W. L. GERMAN, M.SC., PH.D., AND A. I. VOGEL, D.SC., F.I.C.

MOST of the buffer mixtures in use at present on the acid side of neutrality are composed of either carefully standardised hydrochloric acid or sodium hydroxide solution together with substances, such as disodium hydrogen phosphate and citrate, citric acid, borax and sodium carbonate, which contain water of crystallisation (for details see Clark[1] and Britton[2]). It is well known that the preparation and analysis of some of these substances is a laborious and somewhat delicate process. Thus Clark[3] states that the preparation of disodium hydrogen phosphate, $Na_2HPO_4,2H_2O$, necessitates the exposure of the dodecahydrate to the ordinary atmosphere for two weeks, and Kolthoff[4] recommends that commercial borax be recrystallised from water and then preserved in a desiccator over sodium bromide dihydrate in contact with its saturated solution until constant weight is attained. To surmount these difficulties some authors, notably Sörensen and Britton, prepare the salts from weighed quantities of the acids, such as citric acid and boric acid—acids which, be it noted, are themselves not easy to obtain in a high state of purity and of fixed composition—and carbonate-free sodium hydroxide solution.

The present communication describes a series of buffer mixtures covering the *p*H range 1 to 6·3; the substances utilised can be readily prepared and maintained in a high state of purity, and the purity may be readily checked by simple methods. Weighed quantities of acids and salts are employed, and the solutions of differing *p*H are obtained by mixing different volumes of each of the two solutions. No standard acids or bases are required. It should, perhaps, be mentioned that Kolthoff[4] has endeavoured to eliminate the acids and alkalis for buffer solutions; he, however, employs borax and potassium hydrogen phosphates as essential components, both of which possess the disadvantages referred to above. He[4] covers the range of *p*H 3·0 to 5·8 with 0·05 molar succinic acid and 0·05 molar borax mixtures, and the range 5·8 to 9·2 with mixtures of 0·1 molar potassium dihydrogen phosphate and 0·05 molar borax; his values are given to 0·1 *p*H unit only, thus rendering their use in precision work of doubtful value, whilst the volumes of solutions required are given to 0·01 ml., involving, presumably, the use of a micro-burette.

Hydrochloric acid has been universally employed in the preparation of buffer solutions of *p*H 1 to 2 (*cf.* Walpole, Clark and Lubs, Sörensen). Other acids which might be utilised for the same purpose, and which have the great advantage of being solids, are trichloroacetic acid, benzenesulphonic acid, *p*-toluenesulphonic acid and iodic acid. The first two acids are too deliquescent to be of any great use in general practice; iodic acid, owing to its powerful oxidising properties, possesses certain disadvantages and is still under investigation. *p*-Toluenesulphonic acid can be readily prepared or purchased in a state of moderate purity and is comparatively only slightly hygroscopic. The weighing out of quantities of this acid required for buffer solutions presents no difficulties and can be readily carried out without the introduction of any appreciable errors. A method is described in the experimental section whereby the perfectly pure substance is readily obtained. Mixtures of *p*-toluenesulphonic acid and its sodium salt cover the *p*H range 1·1 to 3·3. The range 2·8 to 4·4 employs mixtures of furoic acid and its sodium salt; 3·35 to 5·1 phenylacetic acid and sodium phenylacetate; and 4·8 to 6·3 mixtures of succinic acid and its disodium salt. It will be noted that furoic, phenylacetic and succinic acids are cheap, can be readily purified, and their purity checked by m.p. determinations. The sodium salts can be easily re-crystallised, and be readily obtained anhydrous by heating at 120° C., and the sodium-content is simply determined as Na_2SO_4 by evaporation to constant weight with conc. sulphuric acid in a platinum crucible.

The new buffer solutions are prepared by weighing out the appropriate quantities of the acid and its sodium salt, and dissolving them separately in a definite volume of distilled water. Solutions of any requisite *p*H are then obtained by mixing the necessary volumes of the two solutions measured from a burette.

The work is being extended to a wider range of *p*H by the use of such mixtures as diphenyl guanidine and its salts, sodium diethyl-barbiturate and *p*-toluenesulphonic acid, and it is hoped to communicate these results at a later date.

All the *p*H measurements were made with the quinhydrone electrode and the saturated calomel half cell. Whilst the hydrogen electrode could perhaps be employed for *p*-toluenesulphonic acid, it cannot be used for the other acids, with the exception of succinic acid, owing to the danger of catalytic reduction and consequent drifting potentials. The evidence for the trustworthiness of our results is provided by the agreement within 5 per cent. of the thermodynamic dissociation constants deduced from the buffer solutions with those determined by conductivity methods. The measurements are therefore considered as trustworthy as those which would have been obtained with the hydrogen electrode.

EXPERIMENTAL

PREPARATION OF MATERIALS.—p-*Toluenesulphonic Acid.*—The starting material was either the commercially pure acid or that prepared by the method of Meyer.[5] It was purified as follows:—An almost saturated solution (50 g. in 23 ml. of water) was saturated with hydrogen chloride, the usual funnel device being employed to prevent "sucking back." After several hours the acid crystallised out in the form of colourless prisms. This was rapidly filtered off on a Jena glass sintered funnel, washed rapidly with a little pure concentrated hydrochloric acid and then immediately transferred to a vacuum desiccator containing stick caustic potash and calcium chloride. The solid mass was stirred at periods of 24 hours with a platinum spatula and was dry and analytically pure after 3 to 4 days in the exhausted desiccator. (Found, molecular weight by titration with standard alkali 190·10. Calc. for $C_7H_8O_3S,H_2O$ 190·12.) The solid is somewhat deliquescent, but no difficulty was experienced in weighing out any requisite quantity from a weighing bottle fitted with an externally ground-glass cap. (For a method of working with the extremely deliquescent benzene-sulphonic acid see Jeffery and Vogel.[6])

The substance had m.p. 105–6° in a sealed tube.

Furoic Acid.—The commercial product was recrystallised from boiling water to which some decolorising charcoal was added; it then had m.p. 132–3° C.; 100 g. of the re-crystallised product, 200 g. of absolute alcohol, 200 g. of sodium-dried pure benzene, and 20 g. of pure conc. sulphuric acid were refluxed for 20 hours. After cooling, excess of distilled water was added and the benzene layer was separated. The aqueous layer was saturated with sodium chloride of analytical reagent quality and extracted three times with pure ether. The combined benzene and ethereal extract was washed successively with sodium hydroxide solution until alkaline, then with water and dried with anhydrous sodium sulphate. The ether and benzene were removed and the residue distilled: most passed over at 192°/746 mm. (which fraction was collected separately) and solidified on cooling, m.p. 38° C. The yield of ethyl furoate was excellent. The ester was hydrolysed by refluxing solutions of 60 grams of the ester in 120 g. of rectified spirit and 52 g. of potassium hydroxide (2 mols.) in 104 g. of water for 16 hours and then evaporating to dryness on the water-bath. The residue was triturated with ether to remove unchanged ester, if present, acidified with a large excess of dilute sulphuric acid at 0° C., extracted four times with ether, the ethereal solution was dried with anhydrous sodium sulphate, and the ether was evaporated. The resultant acid had m.p. 131–2° C., and, after re-crystallisation from chloroform, m.p. 132° C.

For most practical purposes re-crystallisation from hot water and then from chloroform is sufficient purification.

Phenylacetic Acid.—This was prepared as described by German and Vogel,[7] and had m.p. 76·5–77° C.

Succinic Acid.—Two samples were employed. One was prepared by the hydrolysis of succinonitrile, m.p. 54° C., with 50 per cent. sulphuric acid and re-crystallised from acetone. The other was of analytical reagent quality and was likewise re-crystallised from acetone. Both samples had m.p. 185–185·5° C.

Sodium Salts.—These were all prepared by adding the calculated quantity of a carefully standardised solution of sodium hydroxide, prepared from the solid, of analytical reagent quality, to known weights of the pure acid and, after evaporation to dryness on the water-bath, were re-crystallised from aqueous ethyl alcohol. They were all dried in an electrically-heated oven at 120° C. for at least 6 hours and then gave theoretical values for the sodium-content.

All solids were kept in vacuum desiccators over calcium chloride until required.

Sodium Hydroxide Solutions.—These were prepared by the electrolysis of analytical reagent sodium chloride with a mercury cathode.[8] The solution was standardised immediately before use against hydrochloric acid of constant b.p., prepared by means of the apparatus described by Jeffery and Vogel,[9] and suitably diluted with equilibrium (conductivity) water by means of a weight pipette.

Quinhydrone.—This was prepared by Biilmann's method,[10] and recrystallised from water at about 70° C. in an atmosphere of nitrogen. One or two days before use, a sample was washed with conductivity water and then dried in a desiccator over calcium chloride.

Calomel Electrode Materials.—The mercury was redistilled, the calomel was prepared electrolytically from the pure mercury and pure hydrochloric acid, and the potassium chloride was of analytical reagent quality. All solutions were made up with conductivity (equilibrium) water.

Apparatus.—The E.M.F. measurements were made with a Cambridge potentiometer reading to 0·1 millivolt, a Tinsley standard Weston cell and a Tinsley mirror galvanometer of high sensitivity. Two Tinsley-Weston cells with N.P.L. certificates were employed as standards; the Weston cell in use with the potentiometer was repeatedly checked against these, but no variation could be detected.

All measurements were carried out in an electrically-controlled oil thermostat at 25 ± 0·01° C. A Bunge balance sensitive to 0·02 mgm. was employed. The weights were directly calibrated against a set recently standardised at the N.P.L. All volumetric apparatus, which was of Pyrex glass, was carefully calibrated before use.

The Pyrex vessel in which the potentiometric measurements were carried out had a capacity of 250 ml., and was provided with four apertures. These were used severally for the saturated calomel electrode, a pair of quinhydrone electrodes sealed through a stopper, and a device for leading nitrogen into the solution; all these fitted into the apparatus with interchangeable ground-glass joints. The stirring device consisted of a tube sealed through a stopper and opening out into a bulb at the lower end; a number of small holes were blown in the bulb, and upon passing nitrogen through the tube a series of fine streams of the gas passed through the liquid, which was thereby efficiently stirred. The nitrogen was derived from a cylinder and was purified by passage through alkaline potassium permanganate solution, conductivity water and purified cotton wool. The stream of nitrogen was stopped immediately before a measurement.

The calomel electrode vessels, in Pyrex, were a modification of Clark's type A[11]; an ungreased, well-ground stop-cock in the arm of the electrode vessel prevented diffusion of the saturated potassium chloride solution into the "measuring" vessel. The electrodes consisted of two bright platinum sheets, 1·2 cm. square, sealed into a glass stopper. Several pairs of these were made and all fitted into the cell by interchangeable, ground-glass joints. The readings of any individual pair employed in the measurements did not differ by more than 0·2 millivolt. After use, they were cleaned by 12 hours' immersion in chromic acid mixture, washed well, left for a few days short circuited in distilled water and then dried in a desiccator. Electrodes which had not been submitted to the last two processes did not give consistent results.

Results.—The *p*H values were computed from the formula:

$$E = E_0 + (RT/F) \log a_H;$$

E_0 the normal electrode potential of quinhydrone at 25° was taken as 0·69969 volt.[12] The potential of the saturated calomel electrode was determined by standardisation against at least two *N*/10 calomel electrodes, for which a value of 0·3376 volt was assumed,[13] and also against Walpole's standard acetate buffers, appropriate correction being made for the temperature coefficient.

The cell employed was:

$$\text{Hg}|\text{Hg}_2\text{Cl}_2,\text{KCl (satd.)}\,||\,\text{buffer solution, quinhydrone}|\text{Pt},$$

and the liquid junction potential was assumed to be negligible.

The first buffer solutions were made up from 50·00 ml. of acid solution, the sodium hydroxide solution of equivalent strength was then added from a carefully calibrated burette (accurate to 0·01 ml.), and the mixture was diluted to 100·00 ml. with conductivity water. The solution was then transferred to the measuring vessel and the *p*H determined after immersion in the oil thermostat for at least two hours.

The results are collected in the following tables. For furoic and phenylacetic acids, the true or thermodynamic dissociation constants were calculated from the formula:

$$pK_{\text{therm.}} = pH + \log([\text{Acid}] - [\text{H}^{\cdot}]) - \log([\text{Salt}] + [\text{H}^{\cdot}]) + 0{\cdot}505\mu^{0\cdot5} - B\mu,$$

where μ is the ionic strength and B is a constant.[14] Now μ is small for the solutions employed, so that the term $B\mu$ was neglected. The mean values of $K_{\text{therm.}}$ for furoic and phenylacetic acids deduced from measurements of the buffer solutions are $4{\cdot}85 \times 10^{-5}$ and $7{\cdot}00 \times 10^{-4}$, respectively; the figures obtained by conductivity are $4{\cdot}884 \times 10^{-5}$ and $6{\cdot}776 \times 10^{-4}$ (unpublished observation), respectively. This agreement within 5 per cent. provides strong independent evidence for the trustworthiness of our measurements.

For the sodium hydrogen succinate—disodium succinate buffers, the true secondary dissociation constant was computed from:

$$pK_{2\text{therm.}} = pH + \log([\text{Acid Salt}] - [\text{H}^{\cdot}]) - \log([\text{Normal Salt}] + [\text{H}^{\cdot}]) + 1{\cdot}515\mu^{0\cdot5},$$

μ was calculated as described by German, Jeffery and Vogel.[15] The mean value thus deduced from the buffer solutions, $2{\cdot}59 \times 10^{-6}$, agrees well with that obtained by direct potentiometric titration of succinic acid and sodium hydroxide ($2{\cdot}54 \times 10^{-6}$).[16]

TABLE I

(1) 50·00 ml. of 0·2 *M* *p*-toluenesulphonic acid monohydrate (38·024 g. per litre) + *x* ml. of 0·2 *M* NaOH; diluted to 100·00 ml.

p*H range: 1·11—2·12*

x	0·00	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00	45·00
*p*H	1·115	1·155	1·206	1·249	1·318	1·396	1·494	1·616	1·798	2·118

(2) 50·00 ml. of 0·1 *M* *p*-toluenesulphonic acid monohydrate (19·012 g. per litre) + *x* ml. of 0·1 *M* NaOH; diluted to 100·00 ml.

p*H range: 1·40—2·22*

x	0·00	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00	45·00
*p*H	1·396	1·423	1·464	1·518	1·579	1·650	1·734	1·843	2·012	2·215

(3) 50·00 ml. of 0·01 *M* *p*-toluenesulphonic acid monohydrate (1·9012 g. per litre) + *x* ml. of 0·01 *M* NaOH; diluted to 100·00 ml.

p*H range: 2·30—3·30*

x	0·00	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00	45·00
*p*H	2·301	2·386	2·436	2·504	2·558	2·646	2·734	2·853	3·029	3·303

(4) 50·00 ml. of 0·01 *M* furoic acid (1·1203 g. per litre) + *x* ml. of 0·01 *M* NaOH; diluted to 100·00 ml.

p*H range: 2·81—4·15*

x	0·00	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00	45·00
*p*H	2·808	2·888	2·976	3·074	3·186	3·299	3·440	3·602	3·810	4·151
$pK_{\text{therm.}}$	—	3·161	3·155	3·153	3·159	3·150	3·156	3·155	3·151	3·157

Mean $pK_{\text{therm.}} = 3{\cdot}155$. Mean $K_{\text{therm.}}$ $6{\cdot}70 \times 10^{-4}$.

(5) 50·00 ml. of 0·01 *M* phenylacetic acid (1·5806 g. per litre) + *x* ml. of 0·01 *M* NaOH; diluted to 100·00 ml.

p*H range: 3·35—5·25*

x	0·00	2·50	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00	45·00
*p*H	3·345	3·449	3·562	3·779	3·966	4·140	4·308	4·473	4·658	4·895	5·250
$pK_{\text{therm.}}$	—	4·310	4·314	4·314	4·310	4·313	4·316	4·312	4·311	4·318	4·323

Mean $pK_{\text{therm.}} = 4{\cdot}314$. Mean $K_{\text{therm.}}$ $4{\cdot}85 \times 10^{-5}$.

(6) 50·00 ml. of 0·01 *M* sodium hydrogen succinate (0·5903 g. succinic acid and 0·8102 g. of disodium succinate per litre) + *x* ml. of 0·01 *M* NaOH; diluted to 100·00 ml.

p*H range: 4·75—6·03*

x	0·00	5·00	10·00	15·00	20·00	25·00	30·00	35·00	40·00
*p*H	4·753	4·970	5·105	5·237	5·359	5·508	5·640	5·810	6·032
$pK_{2\text{therm.}}$	—	5·584	5·590	5·592	5·584	5·596	5·579	5·582	5·587

Mean $pK_{2\text{therm.}} = 5{\cdot}587$. Mean $K_{2\text{therm.}} = 2{\cdot}59 \times 10^{-6}$.

Fig. 1 represents the plots of the six buffer mixtures tabulated above. The curves were drawn on a large scale with the aid of a flexible spline, and the volumes of sodium hydroxide solution corresponding to intervals of 0·10 pH unit interpolated. These were translated into ml. of acid and of sodium salt required to give an equivalent solution. As an example of the method employed, consider the point corresponding to a pH of 4·0 on curve 5. This was prepared by mixing 50 ml. of 0·01 M phenylacetic acid and 15 ml. of 0·01 M NaOH and diluting to 100 ml. In the alternative method of expression of this result, the same solution is obtained by mixing 15 ml. of 0·01 M sodium phenylacetate and adding (50 − 15) = 35 ml. of 0·01 M phenylacetic acid and diluting to 100 ml. The results of these interpolations and recalculations are collected in Table II. It will be observed that for the preparation of any buffer solution, all that is necessary is the preparation of two standard solutions, measuring out the appropriate volumes of each and then diluting to 100 ml. It should be stated that many of these solutions were actually prepared in this way, *i.e.* from solutions of the acid and the sodium salt, and the results were in perfect agreement with those obtained by the use of the acid and sodium hydroxide solutions.

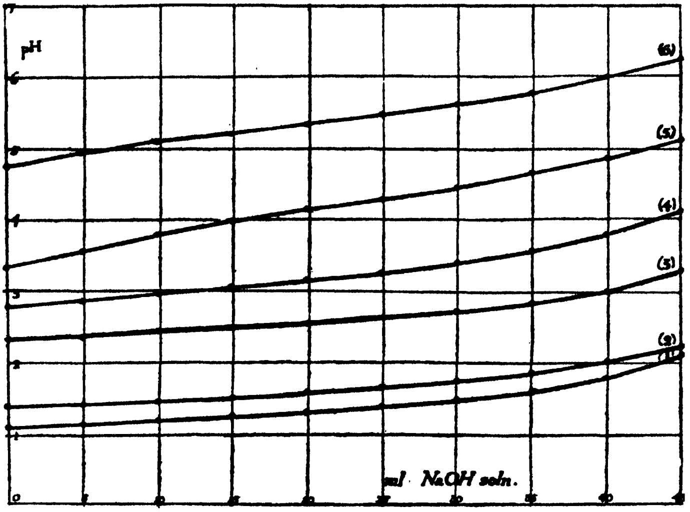

FIG. 1.

TABLE II

COMPOSITION OF MIXTURES GIVING pH VALUES AT INTERVALS OF 0·1 pH AT 25° C.

x ml. of 0·2 M p-Toluenesulphonic acid monohydrate (38·024 g. per litre) and y ml. of 0·2 M sodium p-toluenesulphonate (38·827 g. per litre); diluted to 100·0 ml.

pH	1·20	1·30	1·40	1·50	1·60	1·70	1·80	1·90	2·00
x	42·0	31·6	24·8	18·9	15·35	12·6	11·6	8·7	6·9
y	8·0	18·4	25·2	31·1	34·65	37·4	39·4	41·3	43·1

x ml. of 0·1 *M* *p*-Toluenesulphonic acid monohydrate (19·012 g. per litre and *y* ml. of 0·1 *M* sodium *p*-toluenesulphonate (19·4056 g. per litre); diluted to 100·0 ml.

*p*H	1·40	1·50	1·60	1·70	1·80	1·90	2·00	2·10	2·20
x	48·9	37·2	27·4	19·0	16·6	13·2	10·0	7·6	4·4
y	1·1	12·8	22·6	31·0	33·4	36·8	40·0	42·4	45·6

x ml. of 0·01 *M* of *p*-Toluenesulphonic acid monohydrate (1·9012 g. per litre) and *y* ml. of 0·01 *M* sodium *p*-toluenesulphonate (1·9046 g. per litre); diluted to 100·0 ml.

*p*H	2·30	2·40	2·50	2·60	2·70	2·80	2·90	3·00	3·10	3·20	3·30
x	50·0	44·2	35·8	27·6	21·2	18·5	12·4	10·0	8·0	6·2	5·0
y	0·0	5·8	14·2	22·4	28·8	31·5	37·6	40·0	42·0	43·8	45·0

x ml. of 0·01 *M* Furoic acid (1·1203 g. per litre) and *y* ml. of 0·01 *M* sodium furoate (1·3402 g. per litre); diluted to 100·0 ml.

*p*H	2·90	3·00	3·10	3·20	3·30	3·40	3·50	3·60	3·70	3·80	3·90	4·00	4·10
x	45·2	39·6	34·0	28·4	24·8	21·4	18·0	14·8	12·3	10·1	8·4	6·7	5·4
y	4·8	10·4	16·0	21·6	25·2	28·6	32·0	35·2	37·7	39·9	41·6	43·3	44·6

x ml. of 0·01 *M* Phenylacetic acid (1·3606 g. per litre) and *y* ml. of 0·01 *M* sodium phenylacetate (1·5806 g. per litre); diluted to 100·0 ml.

*p*H	3·40	3·50	3·60	3·70	3·80	3·90	4·00	4·10	4·20	4·30	4·40	4·50	4·60	4·70	4·80	4·90	5·00	5·10	5·20
x	48·7	46·6	44·4	42·2	39·9	37·2	34·4	30·8	28·0	25·1	22·0	19·4	16·9	14·4	12·1	10·2	8·6	7·2	5·7
y	1·3	3·4	5·6	7·8	10·1	12·6	15·6	19·2	22·0	24·9	28·0	30·6	33·1	35·6	37·9	39·8	41·4	42·8	44·3

x ml. of 0·01 *M* Sodium hydrogen succinate (0·5903 g. of succinic acid + 0·8102 g. of disodium succinate per litre) and *y* ml. of 0·01 *M* disodium succinate (1·6203 g. per litre); diluted to 100·0 ml.

*p*H	4·80	4·90	5·00	5·10	5·20	5·30	5·40	5·50	5·60	5·70	5·80	5·90	6·00	6·10	6·20
x	48·8	46·9	44·4	40·4	36·2	32·6	28·6	24·7	21·0	17·6	14·7	12·0	9·9	7·8	5·6
y	1·2	3·1	5·6	9·6	13·8	17·4	21·4	25·3	29·0	32·4	35·3	38·0	40·1	42·2	44·4

BUFFER CAPACITY.—The buffer capacity is expressed by Van Slyke[17] as the differential ratio dB/d*p*H, where dB is the increment (in gram equivalents per litre) of strong base B added to a buffer, and d*p*H is the resultant increment in *p*H. The maximum buffer capacities of our mixtures were as follows:

1.	0·2 *M* *p*-Toluenesulphonic acid and sodium salt	0·21
2.	0·1 *M* ,, ,, ,, ,, ,,	0·12
3.	0·01 *M* ,, ,, ,, ,, ,,	0·0084
4.	0·01 *M* Phenylacetic acid and sodium salt	0·0036
5.	0·01 *M* Furoic acid and sodium salt	0·0056
6.	0·01 *M* Sodium hydrogen succinate and disodium succinate	0·004

The buffer capacity of solutions 3 to 6 is small; such solutions would find application for standardisation of *p*H measurements and for colorimetric work. Their use in biological and biochemical investigations, where a large buffer capacity is usually required, would be limited. For the latter type of investigation accuracy to 0·1 *p*H is usually sufficient; the composition of suitable solutions with larger buffer capacity can be readily calculated in the following manner. Thus, for a monobasic acid:

$$pK = pH + \log([\text{Acid}] - [\text{H}^{\cdot}]) - \log([\text{Salt}] + [\text{H}^{\cdot}]) + 0{\cdot}5\mu^{0{\cdot}5}.$$

If $pH > 4$ and solutions are, say, approximately 0·1 *M*, [H˙] may be neglected in comparison with [Acid] and [Salt], and

$$\begin{aligned} pK &= pH + \log[\text{Acid}] - \log[\text{Salt}] + 0{\cdot}5\mu^{0{\cdot}5}, \\ &= pH + \log(50\text{-}x/x) + 0{\cdot}5\,[\text{Salt}]^{0{\cdot}5}, \end{aligned}$$

where x is the number of ml. of sodium salt solution of the same concentration as the acid required to be added to (50-x) ml. of acid solution to give the required buffer solution

$$\begin{aligned} pK = pH &+ \log(50\text{-}x) - \log x \\ &+ 0{\cdot}5\,[\text{Concentration of } x \text{ ml. of sodium salt}]^{0{\cdot}5}. \end{aligned}$$

As *p*K and *p*H are known, x can be readily calculated.

It must be pointed out that the experiments with the weak organic acids described in this paper were intentionally carried out in dilute solutions in order that the results could be employed in the calculation of their true dissociation constants without the introduction of complex, and at present difficultly soluble expressions, for the activity corrections. The agreement of these values with those determined by independent conductivity methods provides very strong evidence for the trustworthiness of our measurements. Experiments on more concentrated solutions are in progress and will be published in due course.

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Some of the results for phenylacetic acid and a part of the description of the apparatus are reprinted by permission of the Chemical Society.

WOOLWICH POLYTECHNIC
LONDON, S.E.18

Verification of Centrifuge Tubes used for the Determination of Visible Dirt in Milk

BY VERNEY STOTT, B.A., F.INST.P.

INTRODUCTION.—As part of the preliminary work involved in the preparation of the Report of the Dirt in Milk Sub-Committee to the Analytical Methods Committee of this Society and the "British Standard Specification for Centrifuge Tubes and Sedimentation Vessels for the determination of Visible Dirt in Milk, No. 736—1937" (see this Vol. p. 308), the National Physical Laboratory was asked to determine the capacity of the graduated portion of sample centrifuge tubes. This work was carried out in 1932, and the Dirt in Milk Sub-Committee asked the National Physical Laboratory to provide an account of the work for publication. The following notes have therefore been prepared.

PRELIMINARY TESTS.—The preliminary tests were carried out on two Size No. 1 and two Size No. 3 centrifuge tubes, details of the graduated scales of which were as follows:

	Size No. 1	Size No. 3
Capacity corresponding to highest graduation mark	0·02 ml.	0·2 ml.
Equivalent of 1 sub-division	0·001 ml.	0·005 ml.
Tolerance on capacity	±0·0004 ml.	±0·004 ml.

The tolerances represent the maximum permissible error at any point tested and also the maximum permissible difference between the errors at any two points tested.

The object of the work was to ascertain whether the proposed tolerances given above were practicable, *i.e.* whether they were consistent with the degree of accuracy attainable in testing the tubes and with the degree of accuracy attainable in manufacture.

The capacity of the graduated portion of the tubes is defined as follows:

> "The tubes shall be calibrated for content at 20° C., and the capacity corresponding to any graduation mark shall be the volume at 20° C., expressed in millilitres, of the portion of the bore of the tube enclosed between the bottom of the tube and a plane perpendicular to the axis of the tube and passing through the centre of the graduation mark."

It follows from this definition that when any liquid is used for calibrating the tubes, an allowance must be made for the volume of liquid contained in the meniscus.

TABLE I

RESULTS OF TESTS OF FOUR SAMPLE CENTRIFUGE TUBES

		Results of tests with water		Results of tests with mercury		
Identification No. and size of tube A	Graduation mark tested B ml.	Individual observations C ml.	Mean D ml.	Individual observations E ml.	Mean F ml.	Difference D—F G ml.
	0·001*	$0{\cdot}001\ 0_8$ $0{\cdot}000\ 9_1$	$0{\cdot}000\ 9_9$	$0{\cdot}000\ 9_4$ $0{\cdot}000\ 9_8$	$0{\cdot}000\ 9_6$	$+0{\cdot}000\ 0_3$
4971 Size No. 1	0·012	$0{\cdot}011\ 9_2$ $0{\cdot}012\ 0_9$	$0{\cdot}012\ 0_0$	$0{\cdot}012\ 0_0$ $0{\cdot}012\ 0_4$	$0{\cdot}012\ 0_2$	$-0{\cdot}000\ 0_2$
	0·020	$0{\cdot}019\ 9_8$ $0{\cdot}020\ 1_0$	$0{\cdot}020\ 0_4$	$0{\cdot}020\ 0_4$ $0{\cdot}020\ 1_1$	$0{\cdot}020\ 0_7$	$-0{\cdot}000\ 0_3$
	0·001*	$0{\cdot}000\ 7_5$ $0{\cdot}000\ 8_3$	$0{\cdot}000\ 7_9$	$0{\cdot}000\ 8_2$ $0{\cdot}000\ 9_4$	$0{\cdot}000\ 8_8$	$-0{\cdot}000\ 0_9$
4972 Size No. 1	0·012	$0{\cdot}011\ 9_9$ $0{\cdot}012\ 0_2$	$0{\cdot}012\ 0_0$	$0{\cdot}011\ 9_8$ $0{\cdot}012\ 0_1$	$0{\cdot}011\ 9_9$	$+0{\cdot}000\ 0_1$
	0·020	$0{\cdot}020\ 0_3$ $0{\cdot}019\ 9_9$	$0{\cdot}020\ 0_1$	$0{\cdot}020\ 0_6$ $0{\cdot}020\ 0_4$	$0{\cdot}020\ 0_5$	$-0{\cdot}000\ 0_4$
	0·01*	$0{\cdot}008_6$ $0{\cdot}008_6$	$0{\cdot}008_6$	$0{\cdot}008_6$ $0{\cdot}008_9$	$0{\cdot}008_7$	$-0{\cdot}000_1$
	0·03	$0{\cdot}028_8$ $0{\cdot}029_2$	$0{\cdot}029_0$	$0{\cdot}028_9$ $0{\cdot}029_1$	$0{\cdot}029_0$	$0{\cdot}000_0$
4969 Size No. 3	0·12	$0{\cdot}119_4$ $0{\cdot}119_8$	$0{\cdot}119_6$	$0{\cdot}120_4$ $0{\cdot}120_3$	$0{\cdot}120_3$	$-0{\cdot}000_7$
	0·20	$0{\cdot}200_2$ $0{\cdot}200_5$	$0{\cdot}200_3$	$0{\cdot}201_1$ $0{\cdot}201_0$	$0{\cdot}201_0$	$-0{\cdot}000_7$
	0·01*	$0{\cdot}008_2$ $0{\cdot}007_4$	$0{\cdot}007_8$	$0{\cdot}008_0$ $0{\cdot}007_8$	$0{\cdot}007_9$	$-0{\cdot}000_1$
	0·03	$0{\cdot}027_9$ $0{\cdot}027_4$	$0{\cdot}027_6$	$0{\cdot}028_0$ $0{\cdot}028_1$	$0{\cdot}028_0$	$-0{\cdot}000_4$
4970 Size No. 3	0·12	$0{\cdot}119_8$ $0{\cdot}120_2$	$0{\cdot}120_0$	$0{\cdot}120_6$ $0{\cdot}120_5$	$0{\cdot}120_5$	$-0{\cdot}000_5$
	0·20	$0{\cdot}119_3$ $0{\cdot}200_7$	$0{\cdot}200_0$	$0{\cdot}200_9$ $0{\cdot}200_9$	$0{\cdot}200_9$	$-0{\cdot}000_9$

* The sample tubes had a graduation mark corresponding to 0·001 ml. on the Size No. 1 tubes and to 0·01 ml. on the Size No. 3 tubes. It was found desirable, however, to specify in the British Standard Specification that the lowest graduation mark should correspond to 0·002 ml. on the Size No. 1 tube and 0·02 ml. on the Size No. 3 tube.

Each sample tube was tested both with water and with mercury. These two liquids were chosen because they involve quite different meniscus corrections, and so a comparison of the results obtained provides a check on the corrections employed. The weight of water required to fill the tube to the graduation mark under test was determined, and the volume of this water was calculated. The tube being vertical, the water surface was set so that the lowest point of the meniscus was in a plane passing through the top edge of the graduation mark. Great care was taken in making the setting, the meniscus being viewed through a reading microscope, which also served to measure the height of the meniscus and the thickness of the graduation mark. By making appropriate allowance for the meniscus volume, by means of Table III, p. 73, Vol. I, of the International Critical Tables, and for the thickness of the graduation mark, the determined volume of the water required to fill the tube to a given graduation mark was corrected to give the volume of the bore of the tube between the bottom of the tube and a plane perpendicular to the axis of the tube passing through the middle of the graduation mark.

A similar test was made with mercury. In this test the highest point of the meniscus was set so as to be in a plane passing through the lower edge of the graduation mark, the tube being vertical. The necessary allowances for the meniscus volume were made by means of Table I, p. 72, Vol. I, of the International Critical Tables.

The results obtained in the tests are given in Table I, where the volume given against any graduation mark is the volume enclosed at 20° C. between the base of the tube and a plane passing through the middle of the graduation mark and perpendicular to the axis of the tube.

No significance is to be attached to the figures in the last decimal place of the determined capacities. These have merely been inserted to obtain numerically better values in the final difference column G than would have been obtained had the preceding values been rounded off to one decimal place less.

The close agreement between the results obtained with water and those obtained with mercury indicates that appropriate allowances were made for the meniscus corrections. This is made clear by the following details of one of the tests with water and one with mercury on the 0·12 ml. mark on the tube No. 4969:

	Water ml.	Mercury ml.
Volume of liquid determined by weighing	0·122 3	0·118 9
Correction to give required capacity	—0·002 5	+0·001 5
Capacity corresponding to 0·12 ml. mark	$0{\cdot}119_8$	$0{\cdot}120_4$

The uncorrected volumes differ by 0·0034 ml., an amount almost as large as the proposed tolerance 0·004 ml., whereas the corrected volumes agree to within $0{\cdot}000_6$ ml.

Since none of the differences between the mean results obtained with water and those obtained with mercury exceeds 0·0001 ml. on the Size No. 1 tubes, and 0·001 ml. on the Size No. 3 tubes, it follows that the tubes can be tested to an accuracy consistent with tolerances of ± 0·0004 ml. and ± 0·004 ml., respectively. Further, the errors of the sample tubes tested are well within the proposed limits, so that manufacture of the tubes correct within these limits is quite practicable.

SIMPLIFIED METHOD OF TEST.—The procedure adopted in the preliminary work, though necessary to investigate in detail the problems involved, was too elaborate for dealing with any considerable number of tubes in a reasonably short time. Hence the procedure was simplified by adopting mercury for use in the tests, mercury being much more convenient than water for these particular tests, and preparing suitable tables of meniscus corrections to eliminate detailed calculation of corrections for each observation.

For the Size No. 1 centrifuge tubes a mean value of 0·00007 ml. may safely be used for the meniscus correction, *i.e.* the amount to be added to the determined volume of mercury filling the tube to any point on the scale to obtain the volume enclosed between the bottom of the tube and a horizontal plane tangential to the highest point of the mercury meniscus. Variations in tube diameter and meniscus height will not cause variations from the above mean meniscus correction by amounts greater than one-tenth of the permissible tolerance on the capacity of the tube. The tolerance is ±0·0004 ml.

Meniscus corrections for the Size No. 2 tube are given in Table II.

TABLE II

MENISCUS CORRECTIONS FOR THE SIZE NO. 2 B.S.S. CENTRIFUGE TUBE
UNIT = 10^{-3} ML.

Meniscus height		Length of graduated scale from 0·004 ml. to 0·05 ml. graduation mark		
Expressed in terms of sub-divisions on scale	Expressed as difference in scale readings at top and bottom of meniscus	31 mm.	34 mm.	37 mm.
0·1	0·000 2 ml.	0·1	0·1	0·1
0·2	0·000 4 ,,	0·2	0·2	0·2
0·3	0·000 6 ,,	0·2	0·2	0·2
0·4	0·000 8 ,,	0·3	0·3	—

The use of the mean value 0·0002 ml. for the meniscus correction, instead of individual values from Table II, might on occasion give rise to errors of 0·0001 ml., which in general would not be serious in comparison with the tolerance ±0·0008 ml.

Meniscus corrections for the Size No. 3 tube are given in Table III.

The use of the mean value 0·0011 ml. for the meniscus correction, instead of individual values from Table III, might on occasion give rise to errors of 0·0008 ml., which is rather too large to neglect in comparison with the tolerance ±0·004 ml.

The simplified procedure for testing a Size No. 3 tube is to fill the graduated tube with mercury to a point near to the graduation mark to be tested, and to determine the volume of this mercury gravimetrically. In addition, the scale readings corresponding to the top of the meniscus and the line of contact of the mercury with the inside of the tube, respectively, are observed with the unaided eye, and the distance between the 0·02 ml. and the 0·20 ml. graduation marks is measured. On the basis of these last observations the appropriate meniscus correction is obtained from Table III. Taking the scale reading at the top of the meniscus as the nominal capacity at the point tested, then the determined volume of mercury, plus the correction from Table III, gives the true capacity, and the difference is the error at the point tested.

In testing Size No. 1 centrifuge tubes it is only necessary to read the position of the top of the meniscus on the scale to obtain the nominal capacity corresponding to the point tested, and to obtain the true capacity by adding the mean meniscus correction, 0·00007 ml., to the volume of mercury determined gravimetrically.

Size No. 2 centrifuge tubes may be tested either in the same way as Size No. 3 or as Size No. 1, according as to whether it is desired to use individual corrections from Table II or to use the mean correction 0·0002 ml.

TABLE III

MENISCUS CORRECTIONS FOR THE SIZE NO. 3 B.S.S. CENTRIFUGE TUBE
UNIT = 10^{-3} ML.

Meniscus height		Length of graduated scale from 0·02 ml. to 0·20 ml. graduation mark								
Expressed in terms of sub-divisions on scale	Expressed as difference in scale readings at top and bottom of meniscus	36 mm.	37 mm.	38 mm.	39 mm.	40 mm.	41 mm.	42 mm.	43 mm.	44 mm.
0·1	0·000 5 ml.	0·3	0·3	0·3	0·3	0·3	0·3	0·3	0·3	0·3
0·2	0·001 0 ,,	0·5	0·5	0·5	0·5	0·5	0·5	0·5	0·5	0·5
0·3	0·001 5 ,,	0·8	0·7	0·7	0·7	0·7	0·7	0·7	0·7	0·7
0·4	0·002 0 ml.	1·0	1·0	0·9	0·9	0·9	0·9	0·9	0·9	0·9
0·5	0·002 5 ,,	1·2	1·2	1·1	1·1	1·1	1·1	1·1	1·1	1·1
0·6	0·003 0 ,,	1·4	1·4	1·3	1·3	1·3	1·3	1·3	1·3	1·3
0·7	0·003 5 ml.	1·5	1·5	1·5	1·5	1·5	1·4	1·4	1·4	1·4
0·8	0·004 0 ,,	1·7	1·7	1·7	1·6	1·6	1·5	1·5	1·5	1·5
0·9	0·004 5 ,,	1·8	1·8	1·7	1·7	1·6	1·6	1·5	1·5	1·5
1·0	0·005 0 ml.	1·9	1·9	1·8	1·8	—	—	—	—	—
1·1	0·005 5 ,,	1·9	1·9	1·9	—	—	—	—	—	—

These methods have proved satisfactory in testing centrifuge tubes submitted to the National Physical Laboratory for examination. For example, thirty-four Size No. 3 tubes were each tested at three points on the scale, making a total of 102 points tested. In accordance with customary practice at the National Physical Laboratory, each point was tested twice. At only five out of the 102 points tested was the difference between the first and second result in excess of 0·001 ml.—the equivalent of one-fifth of a sub-division or one-quarter of the tolerance ±0·004 ml. Also, at only three points out of a total of 48 points tested on Size No. 1 centrifuge tubes, was the difference between the first and second result in excess of 0·0002 ml.—the equivalent of one-fifth of a sub-division or one-half the tolerance ±0·0004 ml.

The preliminary experimental work was carried out by Mr. C. W. Wells, and I am indebted to Mr. P. H. Bigg for checking the meniscus corrections.

THE NATIONAL PHYSICAL LABORATORY
TEDDINGTON, MIDDLESEX

Erratum: "**The Enzymes of Milk**" (February issue).

P. 88. Delete the tenth line of paragraph (v) and substitute

"are ground intimately together in a mortar, and 0·1 g. of the mixed dye is dissolved in 1 litre of water. For use, 10 ml. of this stock solution . . ."

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

QUININE SULPHATE AS A FLUORESCENT INDICATOR FOR PRECIPITATION REACTIONS

FLECK, Holness and Ward (ANALYST, 1935, **60**, 32) have described the use of substances such as eosin as adsorption indicators of the end-point of reactions involving the titration of silver nitrate with sodium chloride. I have found that quinine sulphate, which is well-known as a fluorescent indicator of certain volumetric reactions, may also be used for precipitation reactions, and that it offers certain special advantages. It is possible that in such cases the quinine sulphate does not behave as a true adsorption indicator, although it enables the correct end-point to be obtained. Its action appears to depend on the fact that quinine sulphate fluoresces in the presence of an excess of some ions but not of others, so that if the end-point of the reaction involves a change from one to another of these types of ions it will be indicated by the production or disappearance of fluorescence.

The technique is very simple. Titration should take place in a thin-walled 200-ml. conical flask, which is supported on a black base in such a position that the filtered ultra-violet falls on it from the side; it is preferable to arrange the lamp so that it is slightly above the level of the liquid in the flask. The solution in the flask should be as concentrated as is conveniently possible, and it should be shaken well after each addition of reagent to stimulate coagulation, as this leaves a supernatant liquid in which the fluorescence can be observed. Only a small pinch of solid quinine sulphate need be used, and a darkened room is not essential if colourless 0·1 *N* solutions are being titrated.

Sharp end-points were obtained by running 0·1 *N* sodium chloride into 0·1 *N* silver nitrate solution, a change from bright pale blue to dull purple being obtained at the end-point. This is in line with the observation that quinine sulphate fluoresces dull purple in sodium chloride, but bright blue in silver nitrate solution. An advantage of the reaction is that it is reversible, so that if the end-point is passed back-titration may be used, although the end-point obtained on titrating in this direction is less sharp. Satisfactory, but less sharp, end-points are also obtained with 0·01 *N* solutions of these reagents.

The end-point is influenced adversely by the presence of nitric acid, and the solution should be neutral to litmus. It is, however, unaffected by many colouring matters, and satisfactory end-points are obtainable by using 0·1 *N* solutions of the reagents in the presence of relatively large quantities (*e.g.* 0·2 per cent. solutions) of caramel, tartrazine, bismarck brown, nigrosine, etc. The method should therefore be suitable for the determination of chlorides in dyestuffs, especially as common salt is used as a diluent for many foodstuff colouring matters.

A novel application is to the volumetric determination of zinc or ferrocyanide by the precipitation method. In this instance quinine sulphate develops its familiar bright blue fluorescence in the presence of sulphate ions, although this disappears when the ferrocyanide ions are in excess. The solutions may be 0·1 to 0·01 *N* in strength, and the general procedure is the same as that described by Treadwell and Hall (*Analytical Chemistry*, Vol. II, 1930, p. 620), except that there is no necessity to add ferrous sulphate. Thus, potassium ferrocyanide is run into the solution of the zinc salt and the mixture is boiled, but the use of an external indicator, such as a uranium salt, is avoided if a pinch of solid quinine sulphate is added; the presence of many colouring matters is without effect on the end-point.

Eosin cannot be used in this case. A sharp end-point is also obtained if the titration is carried out in the cold, but the result is lower than that obtained by Treadwell and Hall's method. It is, however, consistently low, and if the ferrocyanide solution is standardised against a 0·1 N solution of zinc sulphate by the same procedure, the necessity for boiling is eliminated.

JULIUS GRANT

HACKNEY TECHNICAL INSTITUTE
LONDON

TEMPORARY MARKING OF CHEMICAL GLASSWARE

VARIOUS kinds of chemical glassware are provided with an etched or sand-blasted circular spot, on which the user may make some letter, figure or other mark to identify the contents. This obviates the use of grease-pencil on the smooth surface of the vessel—a practice that has certain disadvantages. An ordinary lead pencil is used for writing on the etched spot, and many workers appear to experience difficulty in removing the pencil marks completely. We have found that strong acids, strong alkalis, organic solvents and detergents are of little use for this purpose. It does not appear to be generally known that application of an india-rubber eraser will remove these pencil marks from the etched spots as effectively as from paper.

A. L. BACHARACH

GLAXO LABORATORIES, LTD.
GREENFORD, MIDDLESEX

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

METROPOLITAN BOROUGH OF FULHAM

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1936

OF the 1002 samples examined, 178 were taken informally.

MILK CHOCOLATE CREAM EASTER EGGS.—Two samples, one formal and the other informal, were reported against. These samples contained 10 per cent. of added starch, 18 per cent. of a palm-kernel fat, and 9·6 per cent. of the solids of skimmed milk. The actual amount of shelled, fat-free cocoa was about 4·1 per cent.

ORANGE AND QUININE WINE TONIC.—A sample, labelled "Triple strength," contained only 0·03 per cent. of quinine, whereas ordinary quinine wine contains 0·23 per cent., and a summons was taken out against the vendor.

T. MCLACHLAN

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1936

OF the 4233 samples of food and drugs examined in the year 1936, the number submitted informally was 183.

CRUSHED LINSEED.—A sample of linseed, instead of containing 30 per cent. of oil in accordance with the requirements of the British Pharmacopoeia, contained only 7·36 per cent. The pharmacist was prosecuted and fined 20s.

EXCESS OF ALKALI PHOSPHATE IN FLOUR.—Some cakes and the flour from which they were made were submitted for examination, as they had a bitter taste.

Both were found to contain an excessive amount of an alkali phosphate—a constituent of the self-raising flour. Several samples of flour subsequently taken from the same manufacturer were all of normal composition.

OILED WRAPS.—No conclusive experiments as to the minimum amount of oil that gas store apple wraps should contain appear to have been made in this country, and it is quite possible that wraps containing a smaller amount of oil than hitherto demanded would be effective. One lot of wraps had an odour of paraffin, but it disappeared after the wraps had been used or kept for a short time in store. One of the oils extracted from a quantity of wraps had a lower viscosity, etc. than medicinal paraffin, which is the type of oil usually advocated for impregnating wraps.

HOP RESINS.—Analyses of hops showed that the soft resin contents were somewhat higher than normal. It might have been anticipated that the wet summer would have been conducive to low contents of soft resins, and that the hops would have a low preservative value, but this does not appear to have been the case.

An enquiry has also been made into the sulphur content of hops, and there is evidence that in some instances quantities that might be considered excessive are present.

F. W. F. ARNAUD

Analytical Methods Committee

REPORT OF THE SUB-COMMITTEE ON DIRT IN MILK

(Society of Public Analysts and Other Analytical Chemists)

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A. INTRODUCTION

Constitution of Sub-Committee.—This Sub-Committee was convened by the Analytical Methods Committee and consisted of the following members:—G. D. Elsdon, D.Sc., F.I.C., J. Hanley, M.I.Chem.E., F.I.C., L. H. Lampitt, D.Sc., M.I.Chem.E., F.I.C., H. Lowe, M.Sc., F.I.C., A. More, A.R.C.S., F.I.C., F. W. Richardson, F.I.C., W. H. Roberts, M.Sc., F.I.C., C. J. H. Stock (Honorary Secretary), A. R. Tankard, F.I.C. (Chairman), and J. Wood, M.A., B.Sc., F.I.C. (deceased).

Terms of Reference.—The terms of reference to the Sub-Committee were:

1. What bodies are to be included in term "dirt" or other designation adopted?
2. Method of determining type of origin of dirt.
3. Should dirt be determined by weight, volume, or otherwise?
4. Method of quantitative determination and expression.
5. Applicability of method to decomposed milk.

Number of Meetings.—The Sub-Committee has held 21 meetings, and has carried out a very considerable amount of experimental work in connection with this enquiry.

Experimental Work.

The experimental work has been mainly devoted to the following points:

1. The composition of cow-dung (Appendix No. ii).
2. The method recommended for adoption in the determination of dirt in milk.
3. The isolation of cow-dung added to milk and the determination of the amount recoverable from milk (Appendix No. v).
4. The determination of dirt in samples of dirty milk (Appendix No. vi).
5. The provision of accurately calibrated tubes for measuring the volume of dirt from milk.
6. The effect of centrifuge conditions on the volume of the deposited dirt (Appendixes iv, v and vi).

COMMUNICATIONS.—In response to an invitation inserted in THE ANALYST, various communications were received from analysts in the early stages of the enquiry, and these have been duly considered during the progress of the work.

HISTORICAL.—Various methods for the determination of dirt in milk have been published during the last thirty years. These methods include those involving (1) sedimentation and subsequent centrifuging of the deposit(a); (2) direct centrifuging of the milk in large tubes(b); (3) filtration of the milk and weighing of the washed and dried deposit(c); and (4) various combinations of these operations, and the counting of the deposited dirt particles.(d) The more important of the published papers on the subject describe the sedimentation method of separating the dirt, followed by centrifuging and treatment of the deposit to remove extraneous matters simultaneously brought down with the dirt.

The Sub-Committee has reviewed all these methods, and has given special consideration to method (1). It has also reviewed (a), the Reductase (Methylene Blue) method; and (b), the examination of milk for the *Bacillus coli communis*. The two last-named methods were found to be unsuitable for the purpose in view; whereas method (1), modified as described in this Report, has been experimentally proved to fulfil the requirements of being precise and generally applicable. Moreover, there is evidence to show that, under normal conditions, a general correlation exists between the amount of separable dirt in fresh milk and the numbers of bacteria found in it.*

THE CLEANLINESS OF MILK.—All who have been concerned for a considerable period with the problem of clean milk know well that there has been a great improvement in the cleanliness of milk during the last two decades, both in actual bacterial purity and in the amount of insoluble particulate matter. In part, the more general use of filtering devices is responsible for the improvement for, although no practical form of sieve will remove micro-organisms from milk, the systematic and rapid removal of dung, dropped from the parts of the cow into the milk, undoubtedly prevents the more massive bacterial contamination which follows when large particles of dung disintegrate in milk. For some years past, however, the appearance on the market of graded milks, the influence on dairy farmers of clean milk competitions, and the consequent increased demand from the consumer for clean milk, have greatly expedited this improvement; so much so, that the grosser contaminations formerly found, such as comparatively large amounts of dung and other forms of dirt, are now rarely present even in ordinary commercial milk. The increasing insistence by large suppliers on the cleanness of the raw milk delivered to them by farmers has had a similar tendency. Before any of the factors just mentioned became operative, a decidedly cleaner milk-supply than the average was produced in many areas in this country, and this desirable result was a direct consequence of the work of Houston, Orr, and those public analysts and others who took up the examination of milk for visible dirt, and formulated standards of cleanliness, or limits of contamination by measurable dirt.*

(a) A. C. Houston, 1905, *Report to the London County Council*; T. Orr, 1908, *Report on an Investigation as to the Contamination of Milk* (for various Yorkshire Local Authorities); W. F. Lowe, *Chem. News*, 1912, 61; similar methods by Collingwood Williams; A. R. Tankard, *British Food J.*, 1922, **24**, 51; ANALYST, 1923, **48**, 444; and *ibid.*, 1926, **51**, 31; and others.

(b) R. Eichloff, Abst., ANALYST, 1899, **24**, 33; S. Delépine, 1908 (*Med. Chronicle*); C. Revis, ANALYST, 1909, **34**, 403.

(c) M. Ballo, Abst., ANALYST, 1904, **29**, 154.

(d) S. Barwise and J. White, *J. R. San. Inst.*, 1906, **27**, No. 7, p. 309; A. G. Foulerton, *Rept. to Finsbury Health Committee*, 1907; Thresh and Porter, 1906, *Preservatives in Food and Food Examination*.

* Marshall (*Microbiology*, 1921, p. 466) and the *U.S. Agric. Bulletin* (No. 642, April 30, 1918) both state that under normal conditions there is a fairly direct and close relation between the number of bacteria in milk, and the amount of dirt found by sedimentation. During recent years, however, the increasing use of filters in the cowshed and dairy has destroyed any such relation, as was noticed by T. Orr (*Report on an Investigation as to the Contamination of Milk*, 1908, p. 56).

Only scrupulously clean methods of milk production can result in a satisfactory supply, and the use of sieves where indifferent methods prevail in the cowshed cannot eliminate the objectionable bacterial flora introduced by dirt.

PRINCIPLE OF PROPOSED METHOD.—The particulate matter suspended in fresh milk tends to fall when the milk is at rest. However, a fraction, which may amount to as much as 30 per cent. of the total, is entangled with the fat globules and may rise with the cream. If, after the sediment has been separated, the cream is again mixed with the sediment-free part of the milk, any entangled dirt is freed, and a further fractionation and separation of sediment occurs. The Sub-Committee has proved that the whole of the suspended matters usually met with in fresh milk can be obtained as a sediment if the milk is intermittently stirred during a sufficiently long period of sedimentation. The addition of a preservative during the sedimentation of the dirt is essential to prevent the curdling of the milk. The Sub-Committee has further determined by experiment that the development of some organisms that sink in the milk, resist the subsequent clearing treatment, and thereby give a false indication of the amount of dirt in the sample, is also prevented by the addition of the preservative; also that, while the deposition of dirt is practically complete by the treatment recommended after the first period of 72 hours, it is complete at the end of the second period, and the sample is then free from insoluble matter foreign to milk.

STANDARDISATION OF APPARATUS AND DETAILS OF WORKING.—It has also been found that in order to obtain reasonably close agreement between different workers, the method employed must be standardised in certain essential respects. Thus the need for an accurately calibrated centrifuge tube first made itself felt; then it was found that the compression by the upper layers of a sediment during centrifuging had the effect of reducing the relative volume occupied by the lower layers (see Appendixes iv and v). In order to enable different observers to get comparable results, it was necessary, therefore, to specify the type and size of centrifuge used, the rate and time of centrifuging of the sediment, and the measurement of the volume of the centrifuged deposits in tubes of a standard bore. If workers adhere to these details a reasonably accurate determination of the volume of the dirt in milk can be obtained. The division of a sample of milk containing cow-dung into three parts with equal proportions of dung was also shown to be practicable (see Appendix iii).

ACKNOWLEDGMENTS.—The members of the Sub-Committee wish to place on record their appreciation of the services rendered by the Joint Committee for the Standardisation of Scientific Glassware, the British Standards Institution, and by the National Physical Laboratory, in working out suitable specifications for the sedimentation vessels and centrifuge tubes required for their purpose, and also by the glassware manufacturers in supplying to the Sub-Committee during their work centrifuge tubes calibrated to a high degree of accuracy and greatly superior to any tubes previously obtainable.

B. THE SUBSTANCES TO BE DETERMINED AND THE METHOD OF EXPRESSING THE RESULTS

DESIGNATION OF SUBSTANCES TO BE DETERMINED.—The Sub-Committee recommends that the designation of the substances to be determined by the sedimentation method should be simply "dirt." By dirt is meant all matters insoluble in, and foreign to, milk as it leaves the cow's udder. It may be added that, by the recommended method of procedure for determining dirt in milk, the bulk of the micro-organisms will be removed from the sediment.

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* T. Orr, for example, stated in 1908 that "the imposition of a sediment standard would, in all probability, cause greater care to be taken in the treatment of the milk, both by the farmer and the dairyman" (*Report on an Investigation as to the Contamination of Milk*, 1908, p. 56).

METHOD OF EXPRESSING RESULTS.—The Sub-Committee considers that the amount of dirt should be expressed in parts by volume of moist sediment in 100,000 parts by volume of the sample. It is not usually convenient to record the dirt in terms of dry matter by weight, since the quantities isolated are generally small.

C. RECOMMENDED METHOD FOR THE DETERMINATION OF DIRT IN FRESH MILK

(1) APPARATUS FOR SEDIMENTATION METHOD.—*The Sedimentation Vessel and the Centrifuge Tubes.*—The apparatus consists essentially of a standard glass sedimentation vessel of about 650 ml. capacity gradually tapering at its lower end, to which is attached by suitable means one of the standard centrifuge tubes.* A long stout glass rod, carrying a rubber stopper at one end, is required for stirring purposes, and for closing the main vessel at its lower end while the centrifuge tube is disconnected.

The centrifuge tube may be attached to the sedimentation vessel by means of clean stout rubber tubing (free from detachable powder), the end of the sedimentation vessel fitting loosely inside the mouth of the centrifuge tube; or the centrifuge tube may be ground inside at its open end, to fit the externally-ground lower end of the sedimentation vessel. The British Standard specification, already referred to, requires that the ground-glass joints shall be interchangeable. There should not be, in any part of the apparatus, "ledges" on which particles of dirt may be held up during sedimentation. When a number of determinations have to be made simultaneously, it is convenient to employ a suitable wooden stand holding several vessels and centrifuge tubes (see illustration, Appendix No. vii). When the sedimentation vessels and centrifuge tubes used are connected by rubber tubing, the tubes should not be supported from below, since any upward pressure will cause the lower end of the sedimentation vessel to be tightly engaged and fracture may result. If sedimentation vessels and centrifuge tubes with ground-glass joints are used, the tubes should be supported from below by a spiral spring or suitable collar attached to the lowest shelf of the apparatus stand. By this means fracture of the centrifuge tubes is avoided.

The standard centrifuge tubes, which fit into the holders of the ordinary hand-driven centrifuge, are of three sizes:

No.	1	2	3
Capacity of graduated portion ..	0·020 ml.	0·050 ml.	0·200 ml.
Sub-divisions	0·001 „	0·002 „	0·005 „
Lowest graduation	0·002 „	0·004 „	0·020 „
Approximate bore at graduated part ..	0·9 mm.	1·3 mm.	2·4 mm.

Tube No. 2 is to be used for the measurement of volume of all sediments when the volume comes within the limits of the graduations of that tube; Tube No. 3 may be used for the measurement of larger volumes or, for ease of manipulation, during the process of treatment of large volumes of sediment; and Tube No. 1 may be used when very small amounts of finely-divided deposit are to be measured, or occasionally in the second period of sedimentation described in the method, but the after-treatment of the dirt in such a narrow tube is difficult (see Appendix v).

The centrifuge tubes must be carefully packed into the holders of the centrifuge. The narrow ends of the tubes tend to rupture the metal buckets, with consequent fracture of the tubes, and this is not prevented by the use of so resilient a packing material as cotton-wool. Fibre thimbles or collars should be used to support the tubes at the shoulders, and distribute the strain on the tubes and metal buckets of the centrifuge. (See Appendix vii.)

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* The standard sedimentation vessels and centrifuge tubes are specified in B.S.S. 736—1937, obtainable from the British Standards Institution, Publications Department, 28, Victoria Street, S.W.1. They are of two types, with and without standard ground-glass joints. (See p. 308).

The Standard Centrifuge.—The standard centrifuge used is one capable of a speed of at least 2000 revolutions per minute, and of such a size that the measurement across the machine when in action, from outer tip to outer tip of the whirling tubes, is 10½ inches (26·7 cm.). A larger centrifuge may be employed if a padded wooden block be inserted into each carrier so that the working distance of 10½ inches is still observed. (See Appendix vii.)

Speed of Centrifuge.—Alternatively, if the centrifuge used has not correct measurements, the proper speed shall be determined by calculation, so that the same centrifugal force is obtained at the tips of the tubes as with the standard form of machine. The speed required in any given case may be calculated from the following formula:

$$\text{R.p.m.} = 2000 \times \sqrt{\frac{10{\cdot}5}{d}} = \frac{6500}{\sqrt{d}}$$

where d represents the diameter of swing in inches.

Any form of centrifuge may be used so long as the size and relative speed are maintained; when using the standard machine of the prescribed dimensions, the speed must be approximately, but not less than, 2000 r.p.m. during a five minutes' whirling of the tubes containing the dirt from milk. At speeds appreciably lower than 2000 r.p.m., a higher reading will be obtained, whilst with higher speeds a slightly lower reading may be recorded. From the table of experimental results (Appendix vi) it will be seen that the ratio of the volumes of dirt at speeds of 2000 and 2500 r.p.m. is 100 : 91. It is therefore necessary to adhere closely to the recommended speed, in order to obtain comparable results between different workers. The speed of a hand-driven centrifuge can readily be ascertained; but with electrical and other types of centrifuge, supplied with bubble indicators, it is necessary to calibrate these indicators, or to mark them at the correct level for a speed of 2000 r.p.m. or the equivalent speed calculated as above.

Calibration of the Standard Centrifuge Tubes.—The following note may be useful to those analysts who desire to calibrate their own standard centrifuge tubes.

The method of calibration is fully described in the paper by Verney Stott on "Verification of Centrifuge Tubes used for the Determination of Visible Dirt in Milk" (The Analyst, 1937, 280). The volume of the dirt with its upper surface in the plane of any graduation mark in a tube differs from the volume of a liquid with its meniscus adjusted to that mark by the volume between the meniscus and the plane. If the position marked 0·010 ml. on the tube is to be calibrated, and the weight of water in the tube filled with the meniscus level at the centre of this mark is found to correspond with a volume of (say) 0·0115 ml., then there should be deducted from this latter figure the appropriate meniscus correction for the tube in question (*e.g.* for No. 2 B.S. tube—0·0003 ml.) giving 0·0112 ml. as the corrected reading for volume to the plane of the 0·010 ml. mark. The correction for this tube at the specified mark is therefore +0·0012 ml., to be added to any reading of dirt measured at that mark. The meniscus corrections must be added when the volumes are obtained from measurements made with mercury. The necessary meniscus corrections for water in tubes of various internal diameters can be interpolated from those given in a paper by A. More (The Analyst, 1929, **54**, 630).*

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* The water meniscus corrections for the B.S. centrifuge tubes are:

Tube	1	2	3
Diameter of bore (graduated portion), mm...	0·92	1·32	2·28; 2·39; 2·50
Correction, ml.	0·0001	0·0003	0·0016; 0·0018; 0·0020

Certificates of the National Physical Laboratory for the B.S. tubes state the volumes up to the plane of the centre of the graduation mark. The Sub-Committee recommends the use of centrifuge tubes tested and approved by the National Physical Laboratory.

(2) METHOD.—If desired, a portion of the well-mixed sample is first removed from the bottle for the ordinary chemical analysis. A mark is then made with a grease pencil on the side of the main bottle to indicate the level of the milk left in it, and the volume thus noted (representing that amount of the milk used for the determination of dirt) is subsequently measured when the bottle has been emptied. If a one-pint sample of milk is available, the analyst is recommended to make duplicate determinations of dirt by dividing the sample into two approximately equal portions, taking precautions to ensure that the milk is thoroughly mixed and the dirt uniformly distributed during division. Using the No. 2 centrifuge tube the lowest graduation (0·004 ml.) will represent 2 parts by volume of dirt in 100,000 parts by volume of the milk when 200 ml. of the sample have been used.

Isolation of the Dirt.—To the sample, or to each portion of the sample divided as described, a small quantity of diluted neutralised formaldehyde solution or of filtered potassium dichromate solution is added and thoroughly mixed with the milk. Convenient amounts of these preservatives are 0·2 ml. of 40 per cent. formaldehyde solution in 10 ml. of water, or 0·5 gram of potassium dichromate dissolved in 10 ml. of water, for each 100 ml. of milk. Some of the preserved milk is now poured into a standard centrifuge tube and the milk shaken down so that it completely fills the constricted portion of the tube. This tube is next connected to the sedimentation vessel, the apparatus is fixed vertically in a suitable stand, and the remainder of the milk, kept well mixed, is poured into the vessel. Aeration and the consequent formation of froth should be avoided as far as possible. Finally, the receptacle that contained the sample or portion is washed once or twice with small amounts of water, and the washings are added to the milk in the sedimentation vessel. This is covered with a close-fitting inverted glass dish to prevent access of dust, and the milk is allowed to stand for a minimum period of 72 hours. It is advisable to add a small quantity of ether or petroleum spirit, and to keep a thin layer of the solvent on the surface of the milk during the periods of sedimentation, in order to prevent the holding up of dirt in any separated fatty matter. During the time of standing it is imperative that the milk in the sedimentation vessel be stirred intermittently three times daily, at intervals of four hours, with the rubber-ended glass rod. After each stirring, this rod, and the walls of the vessel above the liquid, are washed down with a small quantity of water into the milk, and the rod is removed during sedimentation. The formation of air-bubbles is to be avoided during stirring, which must be sufficiently thorough to disperse the separated cream throughout the milk and to dislodge any dirt deposited on the tapered sides of the sedimentation vessel.

After the completion of the sedimentation period, the rubber-ended glass rod is lowered into the milk until the stopper engages the narrowest part of the sedimentation vessel. The centrifuge tube attached to the lower end of the vessel is removed, leaving the main quantity of milk in the sedimentation vessel. Some of the milk may then overflow owing to its liberation from the end of the large vessel. In order that no dirt may be lost, any overflowing milk should be caught in a small beaker, and transferred to the centrifuge tube to be used for the second period of sedimentation. As the first centrifuge tube containing the main quantity of dirt will be undesirably full of milk, a portion of this should also be poured off into the second tube, to allow of the centrifuging of the deposit without loss. This second centrifuge tube, with its constricted part completely filled with milk as before, is attached to the sedimentation vessel, the glass rod is withdrawn, and the sedimentation and periodic stirring are continued for a further period of 48 hours or longer.

The centrifuge tube, containing milk and the main part of the sediment, is now transferred to the centrifuge, and the machine spun for two or three minutes at a speed of 2000 r.p.m. A second tube containing milk or water should be placed in the opposite carrier to balance the machine. The centrifuge tube should be closed with a rubber stopper or cap to prevent access of dust.

Treatment of Separated Dirt.—On removing the tube from the centrifuge, the dirt being wholly collected in the graduated portion, the milk in the upper part of the tube is poured off and added to the main bulk in the original vessel. The milk in the constricted part of the tube is also carefully drawn off as far as possible, without disturbing the sediment, by means of a fine platinum wire which, if allowed to impinge on the upper surface of the milk and the side of the tube when the tube is held in a horizontal position, will cause the milk to flow out of the tube. Care should be taken not to produce scratches on the inside of the graduated tube, which may cause breakages in the centrifuge. The upper part of the tube is carefully washed with a small quantity of distilled water to remove any milk, the tube is nearly filled with water, and the sediment is dislodged from the graduated part of the tube and mixed with the water by stirring with the platinum wire, which is then withdrawn and washed. The tube with its contents is submitted to a few minutes' spinning in the centrifuge, by which means all the sediment will again be deposited in the lower end of the tube. The liquid in the wider part of the tube is poured away, and the washing is repeated by adding more water, stirring the dirt up into the water and centrifuging as before. It is essential that all soluble milk solids should be washed away before the next stage of the treatment is begun, and at least three washings with water are necessary.

After as much of the wash-water as possible has been removed by the method already described, a portion of the sediment is examined under the microscope (see "Microscopical Characters of Deposit"). This portion is carefully returned to the tube, and the whole of the sediment is treated for half-an-hour with 2 ml. of cold normal ammonia solution, the sediment being thoroughly mixed with the whole of the reagent by stirring with the wire at once and at intervals of 10 minutes. The tube and its contents are next whirled in the centrifuge for 2 or 3 minutes at a speed of 2000 r.p.m., when the ammonia solution is run off, with the assistance of the wire, but without disturbing the layer of dirt. The contents of the tube are thoroughly washed two or three times with water by stirring, whirling in the centrifuge after each washing, and running off the wash-waters. After removal of the ammonia solution, the dirt is treated in an exactly similar manner with cold normal hydrochloric acid solution for half-an-hour (see next paragraph), with stirring at 10-minute intervals as before. After centrifuging the tube and its contents to collect the dirt in the narrow portion of the tube, the acid is run off and the dirt is again washed with water. These treatments with ammonia solution, water, hydrochloric acid solution, and water again, are repeated, and the dirt is finally washed with water till practically free from chlorides.

In some exceptional cases, a third treatment with alkali and acid may be desirable, but the time of action of the reagents in such instances should be as short as possible. Circumstances may also conceivably arise which make it necessary to modify the procedure of treatment of the sediment by reagents, and the analyst will of course use his judgment. For example, a milk may contain chalk or other material soluble in mineral acid. The treatment of the sediment with hydrochloric acid would here naturally be inadmissible unless the amount of any acid-soluble constituents were ascertained. The use of alkali causes a slight swelling of the sediment, and the subsequent treatment with acid is necessary as a final stage in the operation. Further, it may be found that some curdy matter is deposited especially in the second period of sedimentation, and this may not be readily removable by the usual treatment. In such a case cold normal caustic soda solution, followed by cold normal hydrochloric acid solution and washing with water, may effect the desired separation of the curdy matter from any dirt also present in the deposit.

Measurement of the Dirt.—In order to get a flat (horizontal) surface for measurement, the tube containing the washed dirt and supernatant water is centrifuged in the standard machine for a short time (30 seconds) at about half-speed, the tube turned half-round in its carrier, and the machine spun gently again. If now the surface of the deposit is higher at one side than the other whilst at this loosely-packed stage, it may be levelled by repeating the spinning after the surface layer has been stirred by a rapid twirling, above the sediment, of the platinum wire slightly bent at the end. The tube containing the dirt is then spun in the centrifuge for 5 minutes at approximately, but not less than, 2000 r.p.m. The dirt should now be found as a compact mass at the bottom of the tube, when its volume may be measured. It is advisable to make several readings, stirring up the dirt with the water in the tube before each re-centrifuging and taking the average of the readings. These final measurements must be made immediately on the cessation of the spinning in the centrifuge, or high results may be obtained. The observed reading is adjusted for calibration corrections, and the result is expressed (to the nearest lower half-part) as parts by volume of moist dirt in 100,000 parts by volume of the milk sample under examination.

The additional deposit, if any, obtained during the second period of sedimentation must be treated with the reagents in the same way as the main deposit. As this additional dirt is usually very small in amount, it should either be measured in the No. 1 or No. 2 centrifuge tube or, if too small to reach the lowest graduations in the tubes, it must be added to, and measured with, the main quantity.

If duplicate determinations have been made, the average result should be recorded.

D. DETERMINATION OF THE ORIGIN OF THE DIRT IN MILK

The origin of the dirt isolated from milk may be ascertained by a microscopical examination of the sediment before it has undergone treatment with the alkali and acid reagents (see under "Treatment of Separated Dirt").

MICROSCOPICAL CHARACTERS OF DEPOSIT.—As seen under a medium or low power of the microscope, the "clearing" of the vegetable tissues present (bile-stained or unstained) is characteristic of dung. By "clearing" is meant the absence of the digestible carbohydrates and protein constituents, producing a well-defined appearance of the cellulosic fibrous structures. This, together with yellowish bile-stained vegetable tissues, denotes a manurial origin of those parts of the dirt. Particles of siliceous matter, and fibres of all kinds, may be further differentiated by this preliminary microscopical examination. Dust from forage, byres and roads contains vegetable tissues, manurial debris and siliceous matter. Generally the dirt in milk is a mixture of substances, amongst which may be found dung, some siliceous matter, coal-dust, sooty particles, cloth and cotton fibres, vegetable debris, etc. If the presence of chalk is suspected, one or two particles should be drawn to one side of the slide, and tested for carbonate with hydrochloric acid added from a capillary tube while the particles are in the field of the microscope. In reporting on the examination of milk for dirt, it will usually be sufficient, in our opinion, to record broadly the main constituents of the dirt and, if dung is present, to state that the dirt consisted "partly of dung, and partly of . . .," or "almost entirely of dung, with . . .," as the case may be.

E. DETERMINATION OF DIRT IN SOUR OR DECOMPOSED MILK

The following is a description of a method which has been successfully used by some of the members of the Sub-Committee for the determination of dirt in sour or decomposed milk; further experience of the process may, however, be desirable before it is actually recommended. Occasionally, milk may contain certain organisms, such as *Oidium lactis*, which in their growth during keeping produce structures which deposit with the dirt and are resistant to the chemical treatment recommended for the dirt from fresh milk. In many samples, however, this does not occur, and it is possible to obtain a satisfactory measure of the inorganic and vegetable debris from the dirt in the milk.

(1) GAS-FORMATION IN SOUR MILK.—*Warning*.—The attention of analysts is drawn to the fact that samples of milk which have been kept for some time, especially those which have been contaminated with dirt containing gas-forming bacteria, occasionally develop great internal pressure. Such samples, when kept in bottles the corks of which are held in position with thick coverings of sealing-wax or by means of string, must be treated with great care as the bottles may burst, or if the cork is blown out, a large part of the clotted creamy portion of the uneven sample may be ejected. The sample bottle should be surrounded with a cloth until the internal pressure is relieved (see below).

(2) SUGGESTED METHOD OF DETERMINATION OF DIRT IN SOUR MILK.—The total volume of the sample must first be ascertained. This can be done by weighing the bottle with the sample and, after the milk has been removed as described below, drying the cleaned bottle and weighing it with the cleaned dried original cork and any paper and sealing-wax which may have been removed during the process. The net weight of milk in grams, divided by 1·03, will give the volume in millilitres of milk in the sample. Marking the upper level with a gummed label or grease pencil is sometimes possible, but, in view of the danger mentioned above, a file should never be used for this purpose.

The sample should be examined for foreign particles. If the milk has been shaken up since souring took place, little evidence of deposit may be found, though dark-coloured particles may be seen throughout the sample. Whilst a finger is firmly pressed on the cork to prevent it from being blown out, all sealing-wax (if any) and dust from the cork and outside of the bottle are removed. The internal pressure is released by thrusting a smooth pointed steel wire, such as a hat-pin, between the side of the cork and the neck of the bottle. If there is a tendency for the milk to froth and rise to the cork, the hat-pin is gently moved about, and any exuded milk is caught in a clean beaker. The cork should not be removed until liquid ceases to ooze out. The milk adhering to the cork is washed off into the beaker, and a clean fresh cork, free from holes which may contain dusty matter, placed in the bottle. Three-fourths of the milk is now transferred to a cylindrical separator, and concentrated ammonia solution (sp.gr. 0·880) measured out to an amount about one-tenth the bulk of the milk. A part of this ammonia solution is added to the milk in the bottle and the whole shaken vigorously, taking care that no loss occurs by the cork being blown out, or by liquid or dirt escaping from the bottle. The contents of the bottle are now added to the milk in the separator, and the bottle is washed out with the remainder of the ammonia solution.

The separator must now be shaken vigorously, care being taken to prevent the stopper from being blown out. It is important to break down clots and to form a fine emulsion at this stage, in order to assist separation of the dirt and to obviate unnecessary cleaning of the separated particles from clotted milk at a later stage.

The bottle is then successively washed with clean re-distilled alcohol, ether and petroleum spirit (boiling range, 40–60° C.), measured out in each case in bulk approximately equal to that of the original milk. After each addition of washing liquid to the milk in the separator, the mixture is thoroughly shaken, as in the Gottlieb process, and is finally allowed to stand one hour to permit of separation of the ethereal (fat) layer. By this time, large particles of sediment may show their presence by settling out. The ethereal layer, which is quite free from sediment, is blown off by means of wash-bottle tubes, and set aside. The lower portion of the milk is then drawn off into several stout round-bottomed tubes (about 6 in. by 1 in.), which are closed with clean rubber stoppers, and whirled at a minimum speed of 2000 revolutions per minute for five minutes in a large centrifuge with rigidly-fixed buckets, in which the tubes lie in a nearly horizontal position. The tubes are carefully removed from the machine and, without disturbing the sediment, about two-thirds of the top layer of the milk is poured off into a reserve separator, the tubes filled up again, and the process is repeated until all the alcohol-ammonia-milk layer is treated.

Any emulsion between the milk and the ether layer is retained in the (original) separator, and broken down by shaking with alcohol. The contents of the separator are transferred to one of the 6 in. × 1 in. tubes, to which is added all insoluble matter in the separator, removed by rubbing with a rod and washing with alcohol. The contents of this tube are treated with alcohol and ammonia solution, and spun in a large centrifuge until the dirt is separated.*

Treatment of Separated Dirt.—The main amount of sediment in the large tubes is now concentrated into one tube, in which it is washed twice with water, and all the dirt is then transferred to one of the standard centrifuge tubes. Treatments with normal ammonia and normal hydrochloric acid solutions exactly similar to those adopted with fresh milk are now carried out, and repeated once or twice as found necessary. In some exceptional cases yeasts, moulds or insoluble protein matter may be present, and it may be found almost impossible to free the dirt from these accompanying substances. Treatment with normal caustic soda solution in a boiling water-bath, followed by an acid treatment to counteract the "swelling" effect of the alkali, may assist the clarification in these difficult cases. Care must be taken to heat the tube and its contents gradually in the water-bath, or fracture of the tube may result. After the sediment has been washed with water until free from chlorides, a final centrifugal treatment is given in the standard centrifuge, for 5 minutes, at a speed approximating to but not less than 2000 r.p.m. The volume of moist dirt is expressed as before in parts per 100,000 parts of the milk.

APPENDIXES

(i) INSTRUCTIONS TO SAMPLING OFFICERS IN TAKING SAMPLES FOR ANALYSIS

Before taking the sample the Sampling Officer, with the permission of the vendor of the milk, should stir up the milk in its containing-vessel (churn, hand-can, etc.) with a clean metal plunger, and he should receive the sample in a jug carried for the purpose. Keeping the milk in the jug thoroughly stirred with a large spoon, the Sampling Officer should pour the milk in small quantities at a time successively into each of three bottles provided with funnels, until the whole of the milk has been transferred in approximately equal amounts into the bottles. It is advisable to obtain a 3-pint sample, so that the analyst will receive about one pint of milk, a portion of which may be used for ordinary analysis. The Sampling Officer finally carries out the remaining formalities required by the Act. All the utensils used by the officer should be scrupulously clean, and the sampling and division of the milk should not be done in a dusty atmosphere.

The use of sealing-wax for sealing the cork of the sample bottle is objectionable. A good plan is to wrap the cork in waxed paper before inserting it into the bottle. Cork the bottle in the usual way, notch the cork, and tie it on with tape. Then cover the cork and top of the bottle with a strong paper cap, tie this covering tightly with tape just under the flange on the bottle neck, and finally seal it in two places over the tape, the edge of the paper and the glass bottle neck. All corks used should be free from holes liable to hold detachable dirt or dust.

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* Instead of carrying out the separation of the dirt by centrifuging the liquid in portions in large plain centrifuge tubes, an alternative procedure, which is to be recommended when a centrifuge with rigidly-fixed buckets is not available, is to transfer the lower layer of milk (the alcohol-ammonia-milk layer) into one or more sedimentation vessels such as are used in the fresh milk method, after having fitted a standard centrifuge tube to each of these vessels. The liquid is then allowed to stand, with intermittent stirring, for 3 days or longer, as already described, and the separated dirt is clarified as detailed in the text.

(ii) The Composition of Cow-dung

The composition of dung varies with the feeding, and many different types of dung are included in this Table. An appreciable proportion of the water-soluble matters of fresh dung is rendered insoluble when the dung dries in the air at ordinary temperatures. Allowing for the difference in moisture-content of fresh and air-dried dung, the increase in water-insoluble matters has been found, for 50 samples, to range from 0·9 to 6·8 per cent. (average, 2·7 per cent.), calculated on the fresh dung.

		Fresh dung					Air-dried dung		
Observer	No. of samples	Moisture (loss at 95–100° C.) per cent.	Total solids per cent.	Water-insoluble solids per cent.	Total ash per cent.	Ash in water-soluble solids per cent.	No. of samples	Moisture loss at 95–100° C.) per cent.	Total solids per cent.
1.	3	Max. 89·7	13·8	9·0	—	—	—	—	—
		Min. 86·2	10·3	6·9	—	—	—	—	—
		Aver. 88·2	11·8	7·7	—	—	—	—	—
2.	10	Max. 90·9	17·4	10·4*	—	—	6	Max. 13·3	93·5
		Min. 82·6	9·1	8·7*	—	—		Min. 6·5	86·7
		Aver. 86·6	13·4	—	—	—		Aver. 10·5	89·5
3.	50	Max. 92·4	19·9	13·8	—	—	50	Max. 18·1	89·0
		Min. 80·1	7·6	3·9	—	—		Min. 11·0	81·9
		Aver. 88·3	11·7	7·6	—	—		Aver. 14·0	86·0
4.	3	Max. 91·0	10·6	5·4	—	—	3	Max. 10·0	90·9
		Min. 89·4	9·0	5·0	—	—		Min. 9·1	90·0
		Aver. 90·1	9·8	5·3	—	—		Aver. 9·6	90·3
5.	10	Max. 90·6	13·9	10·7	2·9*	—	10	Max. 11·0	92·6
		Min. 86·1	9·4	8·4	2·3*	—		Min. 7·4	89·0
		Aver. 87·9	12·1	9·6	2·6*	—		Aver. 9·2	90·8
6.		—	—	—	—	—	1	10·4	89·6
8.		—	—	—	—	—	10	Max. 12·3	90·3
								Min. 9·7	87·7
								Aver. 10·9	89·1
9.	4	Max. 90·0	18·3	11·7	3·1	2·0	4	Max. 9·9	92·6
		Min. 81·7	10·0	6·4	2·1	0·8		Min. 7·4	90·1
		Aver. 87·0	13·0	8·5	2·5	1·1		Aver. 8·6	91·4
Totals	80	Max. 92·4	19·9	13·8	3·1†	2·0§	84	Max. 18·1	93·5
		Min. 80·1	7·6	3·9	2·1†	0·8§		Min. 6·5	81·9
		Aver. 88·0	12·0	7·8	2·6†	1·1§		Aver. 12·4	87·6

* On 6 samples only. † On 10 samples only. § On 4 samples only.

(iii) Determination of Dirt in Milk in Three Parts of a Divided Sample

Air-dried dung passed through a 100-mesh metal sieve was added to milk, which was later divided into three equal portions by volume, (A) by an analyst and (B) by an experienced sampling officer. The following were the results obtained by determination of the dirt in the sedimentation apparatus by the Sub-Committee's method:

	A. Milk sample divided by an analyst (One pint divided into three parts)			B. Milk sample divided by a sampling officer (Three pints divided into three parts)		
Portions of milk	Volume of dirt ml.	Parts per = 100,000		Volume of dirt ml.	Parts per = 100,000	
1.	0·037	19·6	Average 20·8	0·038	6·8	Average 6·3
2.	0·040	21·2		0·035	6·3	
3.	0·041	21·7		0·033	5·9	

The quantities of dung added were:

Sample A.—0·030 g. of air-dried dung in 1 pint clean milk.
Sample B.—0·030 g. of air-dried dung in 3 pints clean milk.

(iv) DETERMINATION OF SEDIMENT IN A DUNG SUSPENSION IN 50 PER CENT. GLYCERIN (0·8 g. of air-dried dung per litre)

Vol. suspension taken:	5 ml.	10 ml.	20 ml.	50 ml.
Weight of air-dried dung	0·004 g.	0·008 g.	0·016 g.	0·040 g.
	(Centrifuged water-washed dung recovered)			
Observer	ml.	ml.	ml.	ml.
2.	0·022	0·039	0·074	0·187
5.	0·021	0·036	0·069	0·185
8.	0·019	0·040	0·078	—
9.	0·018	0·036	0·075	0·173
Average ..	0·020	0·038	0·074	0·182
Average ratio: $\frac{\text{g. of air-dried dung}}{\text{ml. of sediment}}$	0·200	0·211	0·216	0·220

The "packing" effect of increasing volumes of sediment is well seen in these results, since, as the amount of sediment increases, the lower layers become more densely packed in the tubes, and the amounts of dirt per unit volume of sediment are not in direct but in increasing proportions.

(See also J. L. McNair and J. F. Hirst, *J. Soc. Chem. Ind.*, 1929, **48**, 127T.)

(v) RESULTS OBTAINED BY THE RECOMMENDED METHOD WITH A SAMPLE OF AIR-DRIED COW DUNG (9·6 per cent. moisture) added to clean milk in proportions of 6, 4 and 2 parts per 100,000 parts of milk, all volumes of moist sediment being measured in tubes of the same bore (2·5 mm.). (0·03, 0·02 and 0·01 g. air-dried dung in 500 ml. milk.)

Air-dried dung added by wt. (per 100,000).	Centrifuged moist sediment found, by volume (per 100,000)							Average height of column of moist sediment (mm.)	Ratio: $\frac{\text{g. of air-dried dung}}{\text{ml. sediment}}$
	Observer 1	2	5	8	9	Mean	Standard deviation		
(*a*) 6·0	31·6	32·0	30·7	25·0	27·0	29·3	3·10	31·0	0·205
(*b*) 4·0	19·4	23·4	20·7	—	18·0	20·4	2·30	21·6	0·196
(*c*) 2·0	11·6	12·2	11·5	10·2	9·6	11·0	1·08	11·7	0·182
(*d*) 1·040	extrapolated from data in first and seventh columns above					6·0	—	6·3	0·173
(*e*) 0·504						3·0	—	3·2	0·168
(*f*) 0·330						2·0	—	2·1	0·165

These results show that the greater the height of column of sediment, the more closely is the sediment packed.

In consequence of this effect, the same quantity of deposit from dung, as used in these experiments, would occupy different volumes in tubes of different bores, *e.g.*:

Tube		B.S. No. 3	B.S. No. 2	B.S. No. 1
Bore (mean) mm. ..	2·50	2·39	1·32	0·92
Vol. of sediment ml. ..	0·200	0·199	0·183	0·169

and, in order to avoid apparent discrepancies from this source in the results of different observers, the Sub-Committee recommends that all volumes of deposit should, where possible, be measured in tubes of the same bore, the British Standard No. 2 tube.

(vi) RESULTS OF THE DETERMINATIONS OF DIRT IN MILK SAMPLES

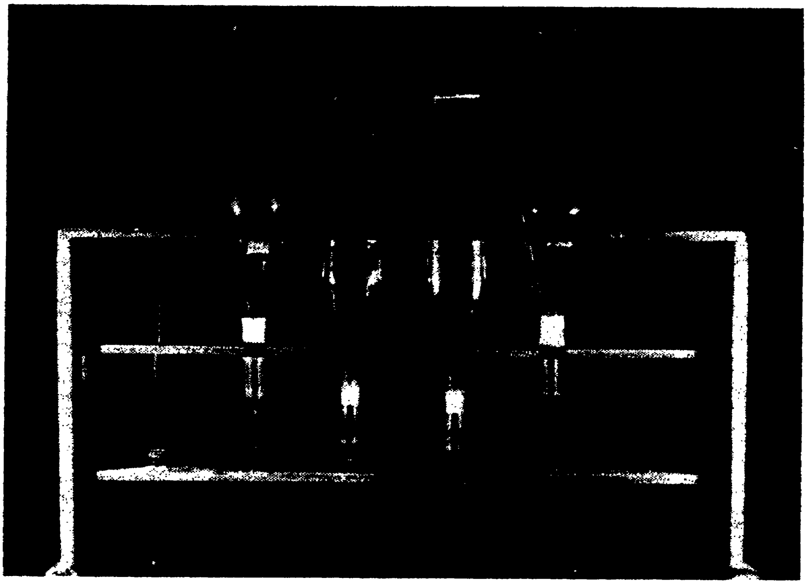
Number of samples	Observer 1	2	3	4	5	6	7	8	9	Mean figure	Standard deviation	Deviation. Percentage of mean Min. −	Max. +	Number of centrifuge tube	Centrifuge revolutions per min.	Method of treatment of Milk	Dirt
	Dirt found in parts by volume per 100,000																
A.1.	5·8	6·6	7·6	5·0	5·6	—	—	7·6	5·1	6·1	0·95	18	25	3	1500*	*a*	*w*
A.2.	5·5	6·6	—	—	6·0	—	—	7·0	5·0								
B.1.	5·4	8·2	7·1	—	4·0	—	4·0	3·8	4·0	5·3	1·86	36	66	3	1500*	*a*	*w*
B.2.	5·7	8·8	6·7	—	—	—	3·6	3·4	4·0								
C.1.	2·6	3·4	2·2	—	3·9	2·4	—	3·5	2·6	3·1	0·57	30	27	2	1500*	*b*	*x*
C.2.	3·3	3·4	2·2	—	3·3	3·4	—	3·8	2·8								
D.1.	1·0	(4·2)	1·3	—	1·4	(2·3)	—	0·9	1·9	1·3	0·36	38	46	2	2000*	*b*	*y*
D.2.	0·8	(4·6)	1·3	—	1·4	1·4	—	1·0	1·9								
E.1.†	6·5	(10·0)	6·2	4·4	—	(9·0)	—	5·5	—	5·8	1·09	31	34	3	2000*	*c*	*y*
E.2.†	5·2	(9·4)	—	4·0	—	6·4	—	4·9	—								
E.3.†	6·0	7·8	7·8	5·0	—	—	—	—	—								
E.4.†	6·4	(10·6)	—	—	5·7	—	—	5·5	—								
E.1.†	—	—	—	—	7·4	—	—	—	7·1	7·0	0·66	10	16	3	2000*	*c*	*z*
E.2.†	—	—	7·6	—	7·5	—	—	—	6·3								
E.3.†	—	—	—	—	6·6	—	—	—	6·4								
E.4.†	—	—	8·1	—	—	—	—	—	6·3								
F.1	10·8	6·1	9·9	9·6	8·7	9·6	6·5	10·5	6·9	8·6	1·54	29	26	3	2000	*c*	*z*
F.2.	9·9	—	7·4	9·8	9·7	6·8	8·5	7·6	7·1								
G.1.	4·8	5·1	7·1	7·0	5·2	3·9	—	3·8	3·7	5·1	1·35	27	39	3	2000	*c*	*z*
G.2.	4·5	5·0	7·7	—	6·2	5·1	—	3·0	4·1	5·1	1·52	41	51	3			
G.1.	4·6	4·7	6·5	6·4	4·2	3·7	—	—	3·3	4·8	1·26	31	35	3	2500	*c*	*z*
G.2.	4·3	4·6	7·1	—	5·6	4·4	—	—	3·7	4·9	1·25	24	45	3			

* Minimum speed.
† Two observers in each laboratory.
a Preserved with "formalin."
b Preserved with dichromate.
c Preserved with dichromate; layer of petroleum spirit.
w Treatment with cold 0·5 *N* NaOH and 0·5 *N* HCl once each for 1 to 2 hours as necessary.
x Three treatments with cold 0·5 *N* NaOH and 0·5 *N* HCl for 1 hour at 20° C.
y Two treatments with cold 1·0 *N* AmOH and 1·0 *N* HCl for ½ hour each.
z As *y*, but with a second period of 72 hours' sedimentation before treatment.

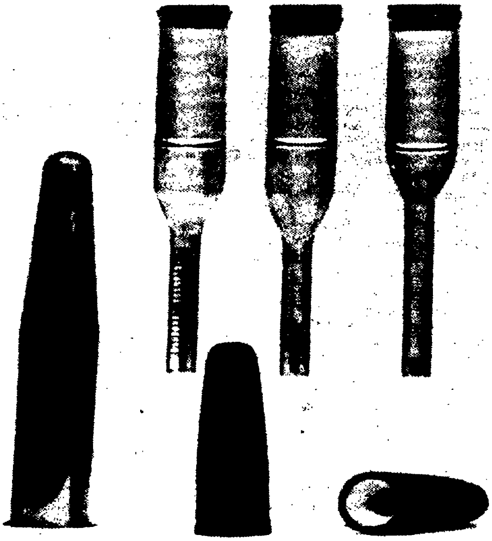
NOTES.—The samples under the same letter (*e.g.* A.1 and A.2) refer to separate portions of the same dirty milk.

The results in brackets have been excluded from the calculations of the means and extreme variations, since they show deviations from the mean greater than twice the standard, indicating some abnormal condition in the tests—probably a slow-running centrifuge.

(vii) APPARATUS FOR THE DETERMINATION OF DIRT IN MILK AS USED BY THE SUB-COMMITTEE.



Sedimentation Vessels, with attached Centrifuge Tubes, with and without Ground-Glass Joints, in Stand to hold 6 Sets of the Apparatus.



Centrifuge Tubes (each shown with 0·02 ml. of Sediment); Centrifuge Bucket and Thimbles.

For and on behalf of the Sub-Committee

(*Signed*) ARNOLD R. TANKARD (*Chairman*)
C. J. H. STOCK (*Hon. Secretary*)

ALLOWABLE LIMIT OF DIRT IN MILK

The Council has endorsed the limits laid down in the following recommendation of the Sub-Committee:

Although it is not within the terms of reference of the Sub-Committee, the members feel that they are in a peculiarly strong position to recommend such a limit. Any proportion of dung in milk, however small its amount, is objectionable, but there are insuperable difficulties in the way of reporting against milk containing dirt unless the quantity can be determined and expressed in figures. The Sub-Committee considers that clean milk, when examined by their recommended method, contains less than 1 part by volume of moist dirt in 100,000 parts by volume of the milk, and that a limit of 2 parts of moist dirt is the maximum which can be conceded, but in stating this opinion they must not be understood to mean that milk containing less than 2 parts of dirt is necessarily a clean milk. In dealing with milk for the purposes of the Food and Drugs (Adulteration) Act, 1928, the Committee suggests, having regard to the degree of variation in the results obtained in their joint experiments, that it would not be desirable to recommend legal action in the case of an isolated sample of dirty milk unless the amount of moist sediment, determined by the recommended method, exceeds 3 parts by volume in 100,000 parts of the sample.

For and on behalf of the Sub-Committee

(*Signed*) ARNOLD R. TANKARD (*Chairman*)
C. J. H. STOCK (*Hon. Secretary*)

Department of Scientific and Industrial Research

WATER POLLUTION RESEARCH BOARD

REPORT FOR THE YEAR ENDED JUNE 30, 1936*

IN the Annual Report of the Water Pollution Research Board it is emphasised that, unless satisfactory methods of treatment and disposal of sewage and industrial effluents are more widely adopted, there will be considerable difficulty in providing the large volumes of water of good quality necessary for domestic, agricultural and industrial purposes.

On the one hand, the demand for water of the highest chemical and bacteriological quality is increasing. This increase is due partly to improved conditions of housing with more general provision of public water supplies, baths, modern sanitary appliances, and hot water and central heating systems. It is also due partly to the development of modern factories in which large quantities of clean water are used in the manufacture and preparation of beverages, foods and other products under more hygienic conditions than formerly.

On the other hand, recent improvement in the trade of some of the older industries, the introduction of new processes and industries, and the development towards centralisation in certain industries, particularly those dealing with agricultural products, have caused increases in the quantities of polluting effluents discharged into rivers in many parts of the country. Difficulties which could have been avoided have arisen in some instances owing to the fact that, in selecting sites and planning factories, adequate consideration was not given to the quantity and quality of the water required for the processes, or to the problems of disposal of the waste waters.

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* Published March 1st, 1937, by H.M. Stationery Office, Adastral House, Kingsway, London, W.C. Pp. 56. Price 1s. net.

The investigations in progress under the Board deal with certain aspects of water supply, with methods of treatment and disposal of sewage and trade waste waters, and with problems of river pollution.

WATER-SOFTENING MATERIALS.—Experiments have been continued on the preparation and properties of materials suitable for softening water by the base-exchange process. Though some of the synthetic products are made in this country, the minerals are all imported. The investigation has shown that satisfactory water-softening materials can be prepared from certain British clays. The material prepared from British fullers' earth is, in fact, superior to the imported treated clays. Several firms are now considering the commercial possibilities of utilising treated fullers' earth for water softening.

SYNTHETIC RESINS AS WATER SOFTENERS.—Earlier work under the Board had led to the discovery that synthetic resins prepared from certain phenolic substances and tannins possess marked base-exchange properties and can soften comparatively large quantities of hard water (*cf.* ANALYST, **1936**, **61**, 33). Unlike synthetic zeolites and treated clays now in commercial use, many of these resins are not detrimentally affected by solutions of acids and alkalis. It has also been discovered that resins possessing acid-exchange properties can be prepared from certain aromatic bases. By treating natural waters first with a base-exchange resin and then with an acid-exchange resin the salts in solution can be wholly removed. These important discoveries have opened a new field of investigation, and experiments on the properties of many examples of the resins have been continued. Some commercial firms are already manufacturing the resins in small quantities.

LEAD IN DRINKING WATER.—The method previously devised (*cf.* ANALYST, **1936**, **61**, 33), as a result of the Board's work, for determining the true average concentration of lead in the drinking water withdrawn from a household service over a period of several weeks has been improved. As originally devised, base-exchange zeolite was used as the filtering medium, but the determination of the lead taken up by the zeolite is a tedious process, and powdered magnesia is now used instead. In this improved form the method has been tried on household services in several towns. The water passes through a meter and then through a filter, containing magnesia and chalk, which takes up the whole of the lead from the water. The quantity of lead taken up by the filter can readily be determined by analysis.

MILK FACTORY EFFLUENTS.—An outstanding advance has been made in the Board's investigation of methods of purification of waste waters from dairies and milk products factories. The importance of finding practicable methods of solving this problem is appreciated by the industry. Through the Milk Marketing Boards the industry is co-operating in the work, and during the past year contributed £3300 towards the cost. The experiments already carried out in the laboratory, and particularly on a large scale at a factory, have demonstrated that it is practicable to purify milk washings, such as those from milk collecting and distributing depots, creameries and condensed milk factories, by the activated sludge process or by biological oxidation in percolating filters operated under certain conditions. Several factories have already installed, or are installing, purification plants designed on the basis of the information obtained in the investigation. In addition to showing how the waste waters can be purified, the investigation has drawn attention to unnecessary losses of milk, cream, buttermilk, skim milk and whey in the wastes. Suggestions have been made, and have been adopted at some factories, for reducing these losses, thus effecting direct savings and reducing the cost of treatment of the effluents.

SEWAGE DISPOSAL.—The report includes a summary of the principal results obtained during the past few years in an investigation of the biology and biochemistry of the activated sludge process of purification of sewage. It also includes the results of recent experiments on physical and chemical aspects of sewage purification.

SILT IN THE MERSEY.—The investigation on the River Mersey, which is being carried out with the object of determining the effect of the discharge of crude sewage on the nature and amount of the solid matter deposited in the estuary, has been continued. The cost is being borne by the Merseyside Local Authorities, the Mersey Docks and Harbour Board, and other interested undertakings.

Available records of various hydrographic surveys of the estuary from 1861 have been studied, and the changes in the estuary from time to time have been ascertained. Estimates have been made of the changes in the quantities of water carried into and out of the estuary during tides of different ranges, that is, in the quantities of water available for scouring the channels in the lower estuary. Numerous records of the quantities of material removed by dredgers operated in the estuary over many years have been examined, with the object of obtaining evidence of any changes in difficulty of dredging. Systematic observations have been made of the velocity of the tidal streams in the estuary, during ebb and flow, over tides of different ranges.

Numerous samples of solid matter from the estuary, from Liverpool Bay and from the bed of the Irish Sea have been examined by physical and chemical methods. For purposes of comparison samples of solid matter from many relatively unpolluted estuaries in England, Scotland and Ireland have also been examined.

ANNUAL REPORT OF THE BUILDING RESEARCH BOARD FOR 1935*

A FEATURE of the Report is the survey of the present position written by Dr. R. E. Stradling, the Director of Building Research. Dr. Stradling considers that until quite recently progress in building research has been derived largely from the development of engineering practice. This fact has tended to produce a wrong emphasis on consideration of strength and stability, while considerations of comfort in the home, office and workshop have, by comparison, been ignored, and there has been a tendency to overlook the part played by walls in excluding moisture and heat or cold. Modern conditions are bringing three problems into prominence, especially in the erection of flats in connection with slum clearance schemes. These are sound insulation, bug infestation and fire resistance.

NOISE.—Tests at the Building Research Station and at the National Physical Laboratory have hitherto dealt with sound transmission through floors, walls and partitions treated separately. The results of the work have, however, focussed attention on the importance of the interaction of the various elements of a building, and an attack is now being made on the problems with the fuller realisation of the importance of treating the building as a whole. Trials are now in progress on a frame building at the Building Research Station based on the principle that the construction should be such as to confine the noise inside the room in which it is made.

BUG INFESTATION.—The survey work carried out by the Station has shown that it is not an exaggeration to say that "virtually every urban authority is more or less troubled with this problem. It is estimated that in many areas practically all the houses are to a greater or less degree infested with bugs." Dr. Stradling urges that the industry should try to make a contribution to the solution of the problem by preventing the formation of cracks in walls, floors and other woodwork and in ceilings, and by producing a form of construction which, in the event of infestation, can be disinfested by the very poisonous gases at present used, without danger to the occupants of surrounding houses.

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* H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3s. 6d. net.

FIRE RESISTANCE.—Considerable advance has been made towards placing the investigation of fire resistance on a scientific basis by the completion of standard definitions for fire resistance by the British Standards Institution and the erection, by the Fire Offices' Committee, of a fire-testing station at Elstree, where full-size building elements can be tested and graded in accordance with the new specification. This station was designed in close collaboration with the Building Research Station, and arrangements have been made between the Department of Scientific and Industrial Research and the Fire Offices' Committee, whereby it is available for a programme of research on fire resistance to be undertaken there under the auspices of the Building Research Board. This programme covers not only the investigation of different forms of construction, but includes tests, on behalf of manufacturers, of proprietary forms of construction, with a view to the issue of certificates of their compliance with the requirements of the various grades in the British Standard definitions.

GRANITE FROM WATERLOO BRIDGE.—The demolition of Waterloo Bridge has provided an opportunity of examining the condition of granite after exposure for 120 years in London. It was found that the outer half-inch of the stone had been affected by its long exposure, for it tended to crumble away in sawing samples for laboratory examination, but there is no reason to suggest that visible signs of decay would have become apparent in the immediate future had the stone remained undisturbed. This bears on the question, not infrequently raised, as to the advisability of re-using old stone. With the more durable stone there is good reason to think that, provided a reasonable thickness of the stone is rejected, old stone should be as durable as new. Specimens of Portland stone taken from St. Paul's Cathedral proved, on laboratory investigation, to be equivalent to the best of the quarry samples now available, except for the surface portions. Detailed investigations on Clipsham stone in connection with the repairs of the Houses of Parliament have shown that the weathering qualities of this stone can now be assessed by laboratory tests, although the method introduced for Bath and Portland stones cannot be applied directly.

CLEANING OF BUILDINGS.—Several proprietary cleaning preparations have been examined in the course of the year. All have proved to be strongly alkaline. It would, therefore, appear opportune to repeat the warning given in previous Reports against the use of chemical aids for cleaning masonry. Acids are sometimes employed for this purpose, but acids are commonly recognised to be dangerous. That alkalis are equally dangerous is not so well understood. In fact, the suggestion is sometimes advanced that the alkali is beneficial, in that it neutralises deleterious acid constituents absorbed from the air; but this suggestion is misleading.

Though their use cannot be given unqualified recommendation even for this purpose, cleaning powders containing alkaline constituents can be used on dense stone, such as marble, without ill effect, provided that the material is thoroughly wetted before the powder is applied and thoroughly rinsed afterwards. But care is necessary to avoid bringing the powder in contact with neighbouring, more absorbent, materials. Examples of the deleterious effects are commonly to be seen in stone walls and door jambs adjoining marble steps. Sometimes the salts can be seen to have penetrated through the walls. In one instance a short flight of marble steps in a corridor was outlined on the main façade of the building by efflorescent salts and a pitting of the surface of the stone. Decay had also occurred on the inner surface.

EFFLORESCENCE OF BRICKS.—Work has been carried out on the effect of firing conditions of the properties of bricks. In tests of the resistance of bricks to disruption by the crystallisation of soluble salts contained in them, it was shown that all specimens fired at temperatures below 900° C. showed only a poor, or moderate, resistance. With one exception, all the clays used showed a satisfactory resistance when fired to 1000° C. or over. It has been found that the liability of brickwork to unsightly white staining due to efflorescence, depends on the amount of soluble magnesium compounds, in particular magnesium sulphate contained in the bricks. The only certain method of eliminating magnesium sulphate from the bricks is to ensure that the minimum firing temperature is over 1050° C.

Corrosive Action of Salt.—Remarkable instances of the corrosion of building structures as a result of the action of common salt were met with. In a margarine factory constructed of re-inforced concrete, corrosion of the steel in the floor beams had taken place to an extent sufficient to burst the concrete and to endanger the structure. Although it was stated that no salt was used in the rooms affected, it seemed probable that this was the cause, and a search was made for a possible source. This ended with the water used for washing the floors, which was obtained from a private artesian well. It was found that sodium chloride contained in this water was the principal agent in the failure. In another building, where salt was found to be responsible for badly corroding electric light conduits, switches, etc., its origin was traced to the sand used in the plaster work, which had been washed with brackish water (containing salt).

Hong Kong

REPORT OF THE GOVERNMENT LABORATORY FOR THE YEAR 1935

In the absence of the Government Analyst, the Report of the work of the Government Laboratory has been drawn up by the Acting Government Analyst (Mr. A. Jackson). The number of samples examined was 3931, as compared with 3728 in the preceding year. Of this total, 1953 were samples of water from public supplies, 330 were chemico-legal samples, and 288 were samples of foods and drugs. Comment is made on the inadequacy of such sampling for a colony of the size of Hong Kong; at least 3000 samples of foods and drugs should be examined annually.

Adulteration of Tea.—Of 21 samples examined 11 were adulterated. This abnormal percentage of adulteration is to be attributed to the demand for a low-priced tea. Among the lower classes tea stalk is a recognised commodity, and several of the samples, reported as adulterated, consisted entirely of stalk.

Counterfeit Coins.—Coinage offences showed a great increase, the number of coins and materials examined increasing from 13 in 1934 to 113. Several of the specimens of coins submitted for analysis were found on persons arrested in places which suggested that the source of these counterfeits was outside the colony. In all these cases it was found that the coins were made of an alloy composed approximately of 5 parts of tin, 2 parts of antimony, and 1 part of copper.

Use of Pepper as a Blinding Agent.—In two cases of robbery with violence pepper was used as a blinding agent. In each case samples of clothing were examined and found to be sprinkled with pepper. In one case parings from the nails of the accused were found to contain structures with all the essential microscopic features of pepper.

Alcohol in Urine.—During the year specimens of urine from persons accused of offences while under the influence of alcohol were examined. In one case a specimen of urine, taken after the accused had been in custody for 24 hours, was found still to contain 50 mg. of alcohol per 100 ml.

International Union of Chemistry

SEVENTH REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

THE Report covers the year ending September 30th, 1936. The following changes in the table of atomic weights have been made:

Carbon, from 12·00 to 12·01
Rubidium, from 85·44 to 85·48
Gadolinium, from 157·3 to 156·9
Lead, from 207·22 to 207·21
Uranium, from 238·14 to 238·07

CARBON.—Baxter and Hale (*J. Amer. Chem. Soc.*, 1936, **58**, 510) determined the atomic weight of carbon by the combustion of hydrocarbons, after purification by crystallisation from hydrocarbon solvents and distillation or sublimation. The average result of all the determinations was 12·009, and, as this is in accord with recent gas density and mass spectrographic evidence that the atomic weight of carbon is not far from 12·01, the International value has been altered to this figure.

RUBIDIUM, GADOLINIUM.—The rubidium value has been based on re-determinations of the ratio RbCl : Ag and RbBr : Ag : AgBr by Archibald, Hooley and Phillips (*J. Amer. Chem. Soc.*, 1936, **58**, 70, 618), and the gadolinium value on the determination of the ratio of gadolinium chloride to silver by Naeser and Hopkins (*J. Amer. Chem. Soc.*, 1935, **57**, 2183); their average result (156·85) is in accord with Aston's recent finding.

LEAD.—Hecht and Kroupa (*Z. anorg. Chem.*, 1936, **226**, 248) have determined the atomic weights of several radiogenic leads, the ratios of the purified lead chlorides to silver and silver chloride being found in the conventional way. The average results for the four materials were 206·079, 206·186, 206·045, and (galena) 207·216. In the light of recent evidence the atomic weight of lead appears to be nearer 207·21 than 207·22, and this change has been made in the table.

URANIUM.—The ratios UCl_4 : 4Ag : 4AgCl and UBr_4 : 4Ag : 4AgBr have been determined by Hönigschmid and Wittner (*Z. anorg. Chem.*, 1936, **226**, 289) on samples of purified uranium material from different sources. The average results were lower than the value in use for some time, which is based on previous work of Hönigschmid and Schilz. The difference is attributed by the authors to the fact that in the earlier work the halides were finally sublimed and fused in nitrogen before weighing. Since the new value, 238·07, best represents the evidence of the whole of the work, it has been adopted for the table.

OXYGEN.—Dole (*J. Amer. Chem. Soc.*, 1935, **57**, 2731) reports a difference in isotopic composition between the oxygen of the air and that of the water of Lake Michigan, U.S.A., corresponding with 0·00008 atomic weight unit, and advocates some single isotope, such as protium, as atomic weight-standard. Since analytical accuracy does not surpass 0·001 per cent., and since the determination of atomic weights by chemical methods must usually involve direct or indirect reference to oxygen, the Committee is still of opinion that no advantage is to be gained by any change of standard at the present time.

HYDROGEN.—Although no change in the atomic weight of hydrogen is made in this year's table, it seems increasingly probable from mass spectrographic measurements (Aston, *Nature*, 1935, **135**, 541; 1936, **137**, 357) that the atomic

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* Authors of papers bearing on the subject are requested to send copies to each of the three members of the Committee: Professor G. P. Baxter, Coolidge Laboratory, Harvard University, Mass., U.S.A.; Professor O. Hönigschmid, Sofienstrasse, 9/2, München, Germany; Prof. P. Lebeau, Faculté de Pharmacie, 4 Avenue de l'Observatoire, Paris (6^e), France.

weight of hydrogen is 0·0002 to 0·0003 higher than the current value. As pointed out by Moles (*Anales Soc. españ, Fis. Quim.*, 1935, 33, 721), chemical determinations have ordinarily been made with electrolytic hydrogen which, owing to isotopic separation, has less than the normal proportion of deuterium.

ANALYTICAL AND CRITICAL REVIEW OF ORGANO-THERMO-CHEMISTRY*

THE First Report of the Commission, published in 1934, is concerned with the determination of the heat of combustion of solid and liquid substances which contain only carbon, hydrogen, oxygen and nitrogen, and the directions given refer only to scientific determinations of the highest precision attainable. For the investigation of combustibles, the determinations have already been simplified in several countries by special Commissions and adjusted to the technical object in view.

In the main part of this second Report the range has been enlarged so as to cover the determination, by means of the calorific bomb, of the heat of combustion of substances containing sulphur or halogens. For the time being, the question can be considered only from a critical and analytical point of view, so that the present publication has a more temporary and advisory character than the first Report. It makes suggestions, draws attention to gaps in our knowledge, and calls for discussion and new researches. The first part deals with the determination of the heat of combustion of substances which contain sulphur or halogens, and the second part with the following subjects: (*a*) The heat of combustion of sulphur compounds; (*b*) fluorine compounds; (*c*) chlorine compounds; (*d*) bromine compounds; (*e*) iodine compounds.

The Commission recommends investigators to vary as much as possible the experimental conditions, and to estimate the probable error of their results; also to record all the analytical and thermo-chemical data required for control or for later re-calculations.

An Appendix gives: I, A table of the isothermal heat of combustion at 0° to 21° C. of benzoic acid, which has been adopted as primary standard substance for the determination of the heats of combustion of solid and liquid substances in the calorimetric bomb. II, Values for the heat of combustion of 1 gram molecule at t° C. of hydrogen gas, which has been selected as primary standard substance for the determination of the heats of combustion of gases and vapours from volatile liquids in the flame calorimeter. III, The value recommended for the heat of formation of dilute nitric acid from gaseous nitrogen and oxygen and from liquid water at 20° C.; also the heats of dilution for solutions of nitric acid. IV, The provisional value for the heat of combustion of succinic acid (1 g. *in vacuo* for an isothermal combustion at constant volume at 20° C.) The Commission, during its meeting in August, 1936, unanimously adopted succinic acid as secondary standard substance for bomb calorimetry. The provisional value is 3025·5 cal., and the final value will be selected when a further series of investigations have become available.

The Report and the Appendix have tables of references to the various subjects discussed.

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[*] *Second Report of the Permanent Commission on Thermochemistry*. Published in German, French and English by the Commission. 1936. General Secretary: 28, Rue Saint-Dominique, Paris.

British Standards Institution

BRITISH STANDARD SPECIFICATIONS FOR READY-MIXED PAINTS (OIL GLOSS)

No. 261—1936. These Specifications, which are issued as one publication, form eight of a series of standard specifications for paints, varnishes and paint ingredients:

Nos. 261.	White ready-mixed paint (white lead base).
262.	Tinted ready-mixed paints (white lead base).
277.	White ready-mixed paints (zinc oxide base).
278.	Tinted ready-mixed paints (zinc oxide base).
293.	Green ready-mixed paints.
294.	Black ready-mixed paints.
295.	Red oxide of iron ready-mixed paints.
371.	Purple brown oxide of iron ready-mixed paints.

The Specifications are divided into three parts, namely: (1) Specific clauses relating to individual paints in respect of composition and specific gravity. (2) General clauses relating to physical properties which are identical for all the paints in the series. (3) Appendixes giving methods of sampling and testing. The compositions detailed in the varied schedules do not define any particular colour. Such definition can only be obtained by reference to a specimen or pattern. The Specification does not purport to supply all the necessary provisions of a contract.

Copies of the Specification may be obtained from the British Standards Institution, Publications Department, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net.

BRITISH STANDARD SPECIFICATION FOR CENTRIFUGE TUBES AND SEDIMENTATION VESSELS FOR THE DETERMINATION OF VISIBLE DIRT IN MILK

THIS Specification (No. 736—1937) has been prepared by the British Standards Institution at the request of, and in co-operation with, the Dirt-in-Milk Sub-Committee of the Analytical Methods Committee of the Society. (See the Report of the Sub-Committee, ANALYST, 1937, p. 287, and V. Stott, *id.*, p. 280.) It is divided into two parts: sedimentation vessels and centrifuge tubes.

The sedimentation vessels are cylindrical in shape, tapering with a steep slope of side to an exit of a size suitable for connection with the centrifuge tubes, either with or without ground-glass joints.

The centrifuge tubes are of a similar shape, but terminate in a constricted portion graduated for measurement of the volume of sediment. The illustrations of these tubes shown in the Report, referred to above, indicate the form of the graduated parts of the tubes. The standard tubes are of three sizes:

Size	No. 1 ml.	No. 2 ml.	No. 3 ml.
Highest graduation ..	0·020	0·050	0·200
Lowest ,, ..	0·002	0·004	0·020
Subdivisions	0·001	0·002	0·005

It is anticipated that analysts may find tubes accurately calibrated in this novel way to be applicable to operations other than the determination of dirt in milk, e.g. determination of dirt suspended in air, suspended matters in sewage, effluents, mineral oils and fuel oils, and for other purposes.

Copies may be had from the British Standards Institution, Publications Department, 28, Victoria Street, London, S.W.1, price 2s. 2d. post free.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Identification of Neutralised Milk. M. R. Baetslé. (*Le Lait*, 1937, **17**, 141–147.)—Neutralised milk may be detected by adding 20 ml. of milk to 30 ml. of methyl alcohol and stirring well three times at intervals. With pure milk, the protein coagulates to form large masses and leaves a clear serum having *p*H between 6·3 and 6·5. Neutralised milk does not coagulate but remains homogeneous for several days. A turbid serum may be obtained by filtration, but the *p*H of this is always above 6·5, and may even reach 8·5 if a large amount of bicarbonate or carbonate has been added. For the determination of the amount of sodium bicarbonate present, the casein may be precipitated by the addition of cold hydrochloric acid. The solution is filtered, the excess of acid is neutralised with ammonia, the phosphates precipitated with uranyl acetate after acidification with acetic acid, the solution is again filtered, and the sodium-content of the filtrate is determined. An alternative method is to evaporate 5 to 10 ml. of the milk and incinerate the residue until a white ash is obtained. The phosphates are removed by heating the ash on a water-bath with 25 ml. of a 2·5 per cent. solution of magnesium acetate, evaporating to dryness, and heating to a dull red. This residue is dissolved in 4 ml. of warm 25 per cent. hydrochloric acid, and the solution is cooled and treated with 10 ml. of ammonia solution, with stirring. The magnesium ammonium phosphate is filtered off and washed with dilute ammonia solution. The filtrate and the wash-liquors are combined and evaporated to dryness on the water-bath, and the residue is dissolved in as little distilled water as possible (maximum 5 ml.). The sodium is precipitated from this solution with uranyl acetate solution. The phosphates may also be removed from the hydrochloric acid solution of the ash by the addition of uranyl acetate, and the sodium may then be determined as the sodium magnesium (or zinc) uranyl acetate, by means of a gravimetric, volumetric or colorimetric method. S. G. S.

Composition of Orange Skins. P. R. v. d. R. Copeman. (*J. Pomology and Agric. Sci.*, 1936, **14**, 205.)—Skins and pulp of Washington navel oranges from trees, some sprayed with lead arsenate and others unsprayed, in the Eastern Districts of the Cape Province were examined. After the juice of the fruit had been expressed and the pulp removed, a weighed quantity of the skin was dried and powdered, a note being made of the initial loss in weight. The sugar-content was determined by extracting the skin with 80 per cent. alcohol, evaporating the solvent, and dissolving the residue in a measured volume of water. The solution was defecated with lead acetate and potassium oxalate, and the sugars were determined by Hanes's modification of the Hagedorn and Jenson method (*Biochem. J.*, 1929, **23**, 99; Abst., ANALYST, 1929, **54**, 349). Both total and reducing sugars were determined, but, on account of the uncertainty regarding the amount of hydrolysis during the drying of the skin, only the total sugar, in terms of invert sugar, was reported. The total pectin was determined by the method of Nanji and Norman (*Biochem. J.*, 1928, **22**, 596; Abst., ANALYST, 1928, **53**, 397). The material was also extracted with 0·5 per cent. ammonium oxalate solution, and the pectin in the extract was determined by the method of Emmett and Carré (*Biochem. J.*, 1926, **20**, 6; Abst., ANALYST, 1926, **51**, 307). Nitrogen was determined by the usual Kjeldahl method. The following results, expressed in terms of grams per fruit, were obtained, *inter alia*.

PULP

Time in days	Invert sugar	Nitrogen	Ash	Potash	Lime	Phosphoric oxide
0	10·5	0·14	0·45	0·21	0·024	0·062
12	11·5	0·12	0·46	0·23	0·027	0·055
48	15·4	0·14	0·51	0·25	0·030	0·048
83	17·1	0·21	0·69	0·37	0·035	0·064
89	16·2	0·18	0·58	0·30	0·029	0·056
Mean (including intermediate values)	14·04	0·15	0·53	0·26	0·028	0·054

SKIN

Time in days	Invert sugar	Nitrogen	Ash	Potash	Lime	Phosphoric oxide
0	4·6	0·14	0·46	0·16	0·14	0·031
12	4·9	0·14	0·47	0·16	0·15	0·025
48	8·5	0·18	0·54	0·18	0·16	0·029
83	9·2	0·17	0·57	0·21	0·14	0·031
89	8·5	0·15	0·51	0·18	0·13	0·029
Mean (including intermediate values)	7·15	0·15	0·50	0·18	0·14	0·027

The amount of pectin in the dry skin was greater, by 1·02 per cent., in sprayed than in unsprayed fruit. As the difference remained constant during the three months, it was thought to be due to differences inherent in the sprayed and unsprayed trees, rather than to the lead arsenate. Similar results were obtained for other factors in the sprayed and unsprayed fruit. The results for the other constituents indicate greater metabolic activity in the pulp than in the skin during the growing period. Except for the lime in the skin and the phosphoric oxide in the skin and pulp, all the factors in both showed an increase during ripening. It is suggested that the lime and phosphoric acid are laid down in the early stages of growth and that their function is more or less structural. The invert sugar increases at a relatively greater rate in the skin than in the pulp. In the skin all the mineral constituents decrease significantly with time and, except for phosphoric oxide, the relative rates of decrease are greater in the dry skin than in the pulp; this suggests that the mineral constituents of the skin are laid down in the early stages of growth. The mean values for pectin agreed well with those of Nanji and Norman (*loc. cit.*). The proportion of lime in the ash of the skin is much greater than in that of the pulp, probably owing to the relationship of the lime to the cell-wall structure of the fruit. There is a close degree of correlation between the ash-content and nitrogen-content of both pulp and skin. It is suggested that the ash may play some part as a carrier of nitrogen. E. B. D.

Decolorisation of Imitation Egg Colouring Matters in Ice-creams on Acidification. K. Brohm and E. Frohwein. (*Z. Unters. Lebensm.*, 1937, **73**, 30–32.)—Yellow azo-dyes, Fast-yellow Y and Tartrazine, used for colouring ice-creams, are decolorised more or less if cream samples containing them become acid. The decolorisation may become so complete that the usual wool-dyeing test for the dyes cannot be applied. The loss of colour is due to reduction of the azo-dyes to primary amines, probably by lactic ferments, for milk samples treated with these dyestuffs showed similar decolorisation on souring. The presence of the amines can be established by diazotisation followed by coupling with sodium β-naphtholdisulphonate (R-salt). Samples which have contained either of the two azo-dyes give a red-brown colour with R-salt, whilst undyed samples give a bright green to yellow colour. Owing to the presence in its molecule of a free amino group, Fast-yellow Y will give the reaction with R-salt without reduction, but the colour is stronger after reduction. The method is as follows:—The R-salt solution is prepared by dissolving sodium β-naphtholdisulphonate in a small quantity of hot 2 *N* sodium hydroxide solution, and diluting the liquid to 20 times its volume with the same alkali solution. A slight brown precipitate settles out, and the clear supernatant liquid is used for the test. Five ml. of the well-mixed sample of ice-cream are mixed with 1 ml. of water, shaken with 3 drops of 2 *N* hydrochloric acid, and treated with 6 drops of 7 per cent. sodium nitrite solution. The liquid is well mixed, but cooling is unnecessary. Five ml. of the R-salt solution are added, and the liquid is again well mixed. The appearance of a red-brown or red-orange colour in the liquid, not in the precipitated proteins, indicates that azo-dyes have been used. Undyed milk never gives a red-brown, but invariably a bright green or yellow colour in the test. E. M. P.

Determination of Fructose with Selenious Acid. G. Reif. (*Z. Unters. Lebensm.*, 1937, **73**, 20–26.)—This is preliminary work on a new method based on the fact that selenious acid, in solutions containing sulphuric acid, can be reduced to selenium by fructose, whilst aldoses have only a slight reducing effect, of the magnitude of a correction. The selenium is weighed as the red modification. The working conditions must be standardised exactly if comparable results are to be obtained, the quantity of selenium precipitated not being proportional to the quantity of sugar, but depending on the concentration of the sugar solution, the composition of the selenious acid—sulphuric acid reagent, and the duration and uniformity of the heating. The selenium reagent is made by dissolving 0·2000 g. of selenious acid in 40 to 50 ml. of water in a 100-ml. flask, adding exactly 10 ml. of conc. sulphuric acid (sp.gr. 1·84) slowly from a pipette, avoiding a large rise in temperature, and making up to 100 ml. with water at room temperature.

The author adopted the following technique:—Ten ml. of sugar solution, containing 0·1 g. or less of sugar, are mixed with 10 ml. of the selenious acid—sulphuric acid reagent in a small conical flask. Two small pieces of porous porcelain (previously boiled in alkali and ignited) are added, and the flask is fitted with a reflux condenser, and stood on a (20-cm.) high tripod with a flat asbestos sheet (22 or 24 cm. in diameter and about 2 mm. thick). The flask is heated over a medium flame in such a way that the liquid reaches boiling-point in 3 minutes, and the boiling is continued gently for 1 hour. Three minutes after removal of the flame the condenser is rinsed with 10 ml. of boiling water. The precipitated selenium and the two pieces of porous porcelain are collected on a weighed porcelain filter, and the flask and filter are washed with 200 ml. of boiling water, the particles of selenium adhering to the walls of the flask being removed with a glass rod tipped with rubber. The two pieces of porcelain are taken out with forceps and washed with part of the 200 ml. of washing water. The precipitate is washed with 10 ml. of alcohol and then with 10 ml. of ether with the aid of suction, and the filter and its contents are dried for 1 hour in a well-evacuated desiccator over phosphorus pentoxide, and weighed. The following table shows that the increment in the amounts of selenium found is not proportional to the increase in the amounts of sugar taken:

Sugar taken	Selenium found in the determination of					
	Fructose	Sucrose	Dextrose	Galactose	Lactose	Maltose
g.	g.	g.	g.	g.	g.	g.
0·01	0·0010	0·0005	0·0001	0·0001	0·0000	0·0000
0·03	0·0027	0·0015	0·0001	0·0002	0·0001	0·0001
0·05	0·0043	0·0023	0·0002	0·0003	0·0001	0·0002
0·075	0·0060	0·0037	0·0003	0·0004	0·0002	0·0003
0·1	0·0076	0·0048	0·0004	0·0006	0·0002	0·0004
0·15	0·0104	0·0070	0·0005	0·0007	0·0003	0·0006

The following results are typical of those in which mixtures of fructose with dextrose, galactose, lactose or maltose were tested:

		Selenium				Selenium	
Fructose +	Dextrose	Calc.	Found	Fructose +	Galactose	Calc.	Found
g.	g.	g.	g.	g.	g.	g.	g.
0·05	0·01	0·0044	0·0044	0·05	0·05	0·0047	0·0046
0·05	0·05	0·0044	0·0045	0·075	0·075	0·0066	0·0064

		Selenium				Selenium	
Fructose +	Lactose	Calc.	Found	Fructose +	Maltose	Calc.	Found
g.	g.	g.	g.	g.	g.	g.	g.
0·03	0·075	0·0030	0·0029	0·03	0·1	0·0032	0·0031
0·075	0·03	0·0063	0·0061	0·075	0·075	0·0065	0·0063

E. M. P.

Organic Acids of Rhubarb (*Rheum Hybridum*). I. Malic Acid of Rhubarb, with a Note on the Malic Acid of Tobacco Leaves. II. Organic Acid Composition of Rhubarb Leaves. G. W. Pucher, H. E. Clark and H. B. Vickery. (*J. Biol. Chem.*, 1937, **117**, 599–603 ; 605–617.)—I. Samples of buds, leaf blades, veins, petioles and rhizomes of rhubarb, variety Victoria, were examined at different stages of growth for total malic acid and for *l*-malic acid, and the values showed agreement within the limits of accuracy of the methods used. The fact that only the laevo-rotatory acid was found is not in accord with the results of Ruhland and Wetzel (*Z. wiss. Biol.*, Abt. E, *Planta*, 1927, **3**, 765; 1929, **7**, 503), who reported the presence of a *dl*-malic acid in rhubarb. This acid may, however, be a different inactive acid, probably not sharply distinguishable from *dl*-malic acid by the methods used, and this view is confirmed by the fact that only the *l*-acid was found in tobacco leaves by the present authors. The various acids, as per cent. of total organic acids, found in (*a*) buds, (*b*) rhizomes of rhubarb were:—oxalic acid, (*a*) 3·6, (*b*) 55·3; malic acid, (*a*) 5·2, (*b*) 3·5; citric acid, (*a*) 26·8, (*b*) 5·6, and unknown acid (by difference), (*a*) 64·4, (*b*) 35·6.

II. Rhubarb leaves were examined from time to time for total organic acid, oxalic, citric, malic and unknown acids. The samples were taken first on April 9 and subsequently on April 30, May 14, June 28 and August 8, and it was found that the acid composition in different parts of the leaf is profoundly influenced by the age of the leaf and by the season in which it has developed. In the young leaves the unknown acid predominates, followed by oxalic acid, whilst in the blades of the leaves developed later in the season oxalic acid predominates over the unknown acid. In the main veins and in the petioles *l*-malic acid is present in greatest amount, followed by oxalic acid, and citric acid and the unknown acids occupy minor positions. Oxalic, citric and the unknown acids occur in a concentration increasing from petiole to vein and blade, but *l*-malic acid in a decreasing concentration, so that the concentration of total acids is not far from constant in all parts of the leaf. This conclusion is not at variance with the results of direct titration of extracts of the tissues. Ammonia determinations in the tissues gave quite low results in every instance, although there was an increase in the leaves of later development, but there was no correlation with individual acids or total acid concentration. D. G. H.

Determination of Amino-Acid Nitrogen in Brewing Materials, with Special Reference to Folin's Colorimetric Method. L. S. Walters. (*J. Inst. Brewing*, 1937, 43, 44–51.)—Sörensen's formol titration method, Van Slyke's gasometric method, and subsequent improvements on them, are critically discussed from the point of view of the brewing industry. The disadvantages of the former are the difficulty in determining the end-point, particularly in dark-coloured liquids, and the lack of selectivity. Disadvantages of the latter are its dependence on slight variations in technique (*e.g.* temperature, duration of the reaction, rate of shaking and presence of alcohol), which is of much more importance with substances encountered in brewing practice than with pure solutions of amino-acids. The manometric method is more accurate, but is expensive and requires specialised technique. The following modification of Folin's method is therefore preferred for worts, beers, and extracts of malt or barley in cold water:—To 25 ml. of sample (diluted to a sp.gr. of 1030° if it is a heavy wort) are added 2 ml. of a 10 per cent. solution of sodium tungstate and 2 ml. of *N* hydrochloric acid, the solution being shaken gently, and, after it has stood for 20 minutes, diluted to 50 ml. and filtered. Re-filtration, or the use of a very retentive paper, may be necessary in order to obtain the bright filtrate which is essential; the filtrate, which is free from proteins, will then keep for at least 1 week. Into two 25-ml. glass-stoppered measuring cylinders are pipetted 1 and 3 ml. of a standard solution of glycine (*vide infra*), and into others are pipetted a range of volumes of filtrate corresponding with 0·1 to 0·3 mg. of amino-acid nitrogen (*e.g.* 1 to 3 ml. for worts, and 2 to 5 ml. for beers or cold water extracts). 0·1 *N* Sodium hydroxide solution is then added until the colour is permanently faint pink to phenolphthalein, then 2 ml. of a buffer solution, and the solutions are diluted to 10 ml. and mixed. The buffer solution consists of a freshly prepared mixture containing equal volumes of 0·1 *N* hydrochloric acid and a solution of sodium carbonate, 8·5 ml. of which are equivalent to 20 ml. of the acid when the titration is carried out with methyl red as indicator. The standard (1 ml. ≡ 1 mg. of amino-acid nitrogen) is prepared by dissolving 0·536 g. of pure glycine (which has been dried in a vacuum over sulphuric acid for some days) in 500 ml. of water, this solution being then diluted to 1 litre with a saturated solution of benzoic acid, which acts as a preservative. The 0·5 per cent. solution of the reagent (1.2.4-naphthoquinone sulphonate), which must conform with Folin's specifications for purity (*cf.* ANALYST, 1922, **47**, 309; 1923, **48**, 79), should be freshly prepared, and 5 ml. are used to produce the colour, which is allowed to develop for 1 hour in the dark. If the sample then shows a colour corresponding with less than 0·1 mg. or more than 0·3 mg. of the standard, the test should be repeated on a more suitable quantity of the filtrate. The solutions are finally stored in the dark for about 30 hours, the contents being then acidified with 1 ml. of a solution containing equal volumes of 50 per cent. acetic acid and 5 per cent. sodium acetate solutions; this intensifies the colour and inhibits the subsequent deposition of sulphur; 5 ml. of a 4 per cent. solution of sodium thiosulphate are added to destroy any surplus quinone. The mixtures are diluted to 25 ml., and the brown-red colour is matched colorimetrically, preferably in a Duboscq type of instrument, after 10 minutes but within 1 hour, as sulphur may separate. The results are usually reproducible to within 3 or 4 per cent. and are comparable with those obtained by a standardised form of Van Slyke's micromethod, although 15 to 25 per cent. lower than those found by Kolbach's modification of Sörensen's method; the method takes 30 hours for completion, but the actual time required for manipulative work is small. Ammonia interferes, since it reacts in the same way as an amino-acid, but the quantities present in brewing materials are usually too small to be of significance; alternatively, it may be removed by distillation or by permutit. J. G.

Detection and Quantitative Determination of Glycerol in Marzipan and Persipan.* **H. Kluge.** (*Z. Unters. Lebensm.*, 1937, **73**, 34–38.)—Marzipan and persipan are liable to be adulterated with glycerin. For its detection 10 to 20 g. of the powdered sample are rubbed to a dry powder with anhydrous sodium sulphate and sand, and vigorously shaken with anhydrous, freshly distilled acetone in a 300-ml. conical flask. The mixture is heated and allowed to stand overnight, the acetone solution is filtered, the filtrate is evaporated in a glass dish on the water-bath, and the residue is dried at 70° C. for half-an-hour. The oil is removed by shaking with a few ml. of low-boiling petroleum spirit, the petroleum solution is filtered off, and the residue and the filter are washed twice with small quantities of the solvent. The petroleum spirit is completely evaporated from the residue, which is then treated with acetone, and the acetone solution (2 to 3 ml.) is evaporated almost to dryness in a test-tube on the water-bath; the residual acetone is removed in a current of air from a hand bellows. A small amount of potassium bisulphate is added to the residue, and the test-tube is heated over a Bunsen flame until white vapours are emitted. A glass rod dipped in freshly prepared reagent made by adding 3 drops of piperidine to 20 drops of a 1 per cent. sodium nitroprusside solution is held in the vapour. If glycerol is present, the acrolein in the vapour produces a blue colour in the drop of reagent; a piece of paper dipped in the reagent may be used instead of the glass rod. This test will detect 0·1 per cent. of glycerin in the marzipan or persipan.

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* *Marzipan* is defined as a mixture of blanched sweet almonds ground up while moist with heated sugar in an amount not exceeding 35 per cent. Up to 5 per cent. of dextrin syrup may be added to keep the mass moist. Marzipan products should consist of 1 part of marzipan with up to 1 part of sugar. *Persipan* is the analogous product made from blanched, de-bittered apricot and peach kernels (*cf. Z. Unters. Lebensm.*, 1927, **54**, 78, 89. Abst. ANALYST, 1927, **52**, 716).

The method for the quantitative determination, based on the isopropyl iodide method of Zeisel and Fanto (*cf.* ANALYST, 1902, **27**, 300), is as follows:—Ten g. of the powdered sample are rubbed to a fine powder with anhydrous sodium sulphate and sand, and the mixture is extracted with anhydrous, freshly distilled acetone for 6 hours in a Soxhlet apparatus. The acetone is evaporated, and the residue is dried for half-an-hour at 70° C., most of the remaining acetone being then removed in a current of air from a hand bellows. The warm dry residue is shaken vigorously with 49·5 ml. of water, 0·5 ml. of Merck's dialysed iron solution is added, and the liquid is again shaken; about 3·5 g. of sodium chloride are added to effect the "salting out." The mixture is filtered, and the glycerol in the filtrate is determined in the apparatus used in the official (German) method of testing wine. Five ml. of the filtrate and 15 ml. of hydriodic acid of sp.gr. 1·96 are put into the boiling flask, and the washing flask is charged with 5 ml. of red phosphorus (purified by repeated washing with potassium iodide—iodine solution and water and tested in a blank experiment). The precipitation flask contains 50 ml. of a clear alcoholic silver nitrate solution (prepared by dissolving 20 g. of silver nitrate in 50 ml. of water and making up to 500 ml. with absolute alcohol). Pure dry carbon dioxide is led through the apparatus at the rate of about 3 bubbles per second, and the boiling flask is heated in a bath of metal or phosphoric acid, so that its contents boil slowly; the condensation ring should not rise more than half way up the distillation tube. After about 2 hours the heating is stopped, and the silver nitrate solution and the precipitate of silver iodide are transferred to a 600-ml. beaker, treated with 10 to 15 drops of dilute nitric acid, and heated on the water-bath for half-an-hour. The liquid is cooled in the dark, and the silver iodide is collected on a dried, weighed, asbestos Gooch crucible, washed with water containing nitric acid, then with water, and finally with alcohol, dried at 130° C., and weighed. The weight of the silver iodide, multiplied by the factor 0·393, gives the weight of the glycerol, and this weight multiplied by 100 gives the percentage of glycerol in the sample.

The following method may be used as an alternative to extraction in a Soxhlet apparatus:—Ten g. of the sample are rubbed with anhydrous sodium sulphate and sand and boiled on a water-bath under reflux for 10 minutes in a 300-ml. conical flask with exactly 100 ml. of anhydrous, freshly distilled acetone. The flask is thoroughly cooled in water, without disconnecting the reflux condenser, and the contents are filtered through a pleated filter-paper, 15 cm. in diameter, the funnel being covered with a large watch-glass. Fifty ml. of the filtrate are dried in a dish on the water-bath, and then for half-an-hour at 70° C., and the determination is carried out as described above. The weight of glycerol is multiplied by 200 to give the percentage of glycerol in the sample. This extraction method is almost as accurate as the Soxhlet extraction.

To test the accuracy of the method, it was applied to almonds and apricot-kernels, and also to marzipan and persipan free from glycerin and with 1 per cent. and 5 per cent. of commercial glycerin (0·82 per cent. and 4·1 per cent. of pure glycerol). The results were:

Sample	Glycerol found Per Cent.	Error Per Cent.
Kernels	0	
Pure marzipan	0	
Pure persipan	0	
Marzipan or persipan+1 per cent. of glycerin..	0·88	+0·06
Marzipan+5 per cent. of glycerin	4·07	—0·03
Persipan+5 per cent. of glycerin	3·82	—0·28

Glycerin is to be regarded as an adulterant, as large additions give the product an unpleasant pasty taste, and small quantities, such as 1 per cent. or less, have not been found to confer improved keeping qualities. E. M. P.

Simplified Method of Potentiometric Titration. E. H. T. Jukes. (*J. Inst. Brewing*, 1937, **43**, 80–81.)—The method of Callan and Horrobin (*J. Soc. Chem. Ind.*, 1928, **47**, 329) is adapted to brewery work. Two similar quinhydrone electrodes are prepared in the usual way from clean platinum wire; one is immersed in a beaker containing 25 ml. of the acid liquid to be titrated, and the other in a beaker containing 15 ml. of a buffer-solution having the same *p*H as the end-point of the reaction in question. The two solutions are connected by means of an H-shaped tube containing a saturated solution of potassium chloride, leakage being prevented by closing the lower ends of the side-limbs with plugs of filter-paper, and by joining the corresponding upper ends by rubber tubing. The two electrodes are connected in series with a tapping key and a dead-beat, centre-zero type of galvanometer (resistance 950 ohms, and sensitivity 25 scale-divisions per micro-amp.). Quinhydrone is added to the contents of each beaker, and on titration of the sample the end-point is indicated when the galvanometer shows no deflection; the tapping key should be depressed only momentarily so as to avoid polarisation, and for *p*H values over 8 the quinhydrone electrodes must be replaced by hydrogen or other suitable electrodes. The apparatus is cheap and easily assembled, and the method is rapid and very suitable for coloured liquids. For determinations of the acidity of sour beer a phosphate buffer of *p*H 7 should be used, and an allowance made (by means of a trial titration) for the natural acidity of the finished beer (*p*H 4); the sensitiveness is then at least 0·1 ml. J. G.

Detection of Small Amounts of Butter-fat in Coconut Oil. J. Grossfeld. (*Z. Unters. Lebensm.*, 1936, **72**, 434–435.)—It has been shown (Grossfeld and Battay, *Z. Unters. Lebensm.*, 1931, **62**, 122; Abst., ANALYST, 1931, **56**, 750) that coconut oil contains a small amount (0·61 per cent.) of caproic acid. This amount, having a titration value of 1·7 ml. of 0·1 *N* alkali for 5 g. of fat, renders the detection of small amounts of butter-fat in coconut oil difficult. More recently von Fellenberg (*Mitt. Lebensmittelunters. u. Hyg.*, 1936, **27**, 133) has found acetic acid in coconut oil in amounts corresponding with a titration value of 0·08 to 0·10 ml. of 0·1 *N* alkali in 5 g. of fat. Since, in the determination of the butyric acid value of the fat, only a fraction of the acetic acid present distils over, the amount found is wholly within the limits of experimental error. The butyric acid value of coconut oil is therefore due to the caproic acid present. Since coconut oil is used in the manufacture of many kinds of margarine, the detection of small amounts of milk-fat in it is of importance, as, for example, to determine whether whole milk, or skimmed milk, or water, has been used as mixing material in pastry made with margarine. For the experiments, coconut oil was mixed with small amounts of butter-fat, and the butyric acid value of the mixture was determined by the semi-micro method of Grossfeld (*Z. Unters. Lebensm.*, 1932, **64**, 436). The results found were compared with the butyric acid value calculated for the mixtures used. The average error was ± 0·1. For the calculation of the amount of butter-fat from the butyric acid value in the presence of large amounts of coconut oil, another characteristic value is required. Instead of the saponification value previously employed, Grossfeld (*loc. cit.*) has employed the more conveniently determined and more specific total lower fatty acid value. From this the butyric acid value is deducted to give the "residual value." The amount of milk-fat present is then given by the expression $5{\cdot}12B-0{\cdot}12R$ where B is the butyric acid value and R the residual value. The results of the application of the method to mixtures of coconut oil with from 0·8 per cent. to 11·3 per cent. of butter-fat are given. The average difference between the amount of butter-fat found and that known to be present was ± 0·3. A. O. J.

Characteristics of the Fat of Yeast (*Saccharomyces* spp.). K. Täufel, H. Thaler and H. Schreyegg. (*Z. Unters. Lebensm.*, 1936, **72**, 394–404.)—Yeast-fat forms the basis of a commercial preparation known as "Cerolin" prepared by the extraction of purified brewers' yeast with alcohol. The sample examined was a dark brown, unctuous substance with an odour of stale beer, and contained yeast cells as impurity. After purification with ether it gave the following results:—Acid value 108·4, saponification value 156·6, ester value 48·2, Reichert-Meissl value 7·4, Polenske value 3·4, iodine value (Hanus) 130·4, unsaponifiable matter 19·6 per cent., total fatty acids 66·4 per cent., glycerol (Willstätter-Madenaveitia method: *cf.* ANALYST, 1912, **37**, 571) 5·3 per cent. It is uncertain whether the free acids indicated by the high acid value are characteristic of yeast-fat or are introduced during manufacture by hydrolysis or decomposition. The latter hypothesis appears the more probable. The fatty acids were separated into solid and liquid fractions by the methods of Twitchell (*Ind. Eng. Chem.*, 1921, **13**, 806; Abst., ANALYST, 1921, **46**, 466) and of Bertram (*Chem. Weekblad.*, 1927, **24**, 489; Abst., ANALYST, 1927, **52**, 489). By Twitchell's procedure 23·1 per cent. of the total fatty acids were obtained as solid saturated acids and 76·1 per cent. as liquid unsaturated acids. The solid acids had the following characteristics:—Neutralisation value 210·1, mean molecular weight 267·0, iodine value (Hanus) 2·4. The liquid acids gave: neutralisation value 198·3, mean molecular weight 282·9, iodine value 95·1. From a consideration of the total amount of liquid acids, it is concluded that only a small amount of highly unsaturated acids (linolic and linolenic) is present. This conclusion does not agree with the results of Neville (*Biochem. Z.*, 1913, **7**, 341) or of Warden (*Amer. J. Physiol.*, 1921, **47**, 454). Separation of the solid acids by Bertram's method (*loc. cit.*) yielded 27·2 per cent. of solid acids of neutralisation value 202·6 and mean molecular weight 276·9. By fractional distillation of their ethyl esters the solid acids (separated by Twitchell's method) were found to consist of palmitic and stearic acids, and no confirmation of the presence of arachidic or lauric acid was obtained. The volatile acids consisted of valeric acid (probably derived from the proteins of the yeast rather than from the fat), caprylic, capric and lauric acids. The liquid fatty acids contained oleic acid and linolic acid in small amount, but there was no evidence of the presence of linolenic acid. The unsaponifiable matter of yeast-fat was a bright yellow semi-solid substance, which when fractionally crystallised from alcohol was separated into ergosterol and another sterol which appeared to be cryptosterol. By precipitation as digitonides the total amount of sterols was found to be 3·3 per cent. of the fat. The remaining 16·3 per cent. of unsaponifiable matter proved to be squalene, to which the high iodine value of yeast-fat is to be attributed. Squalene, once considered to be peculiar to the shark-liver oils, has been found in olive oil (Thorbjarnarson and Drummond, ANALYST, 1935, **60**, 23). The quantitative composition of the sample of yeast-fat was as follows:—Glycerol, 5·3; acids volatile in steam, 5·2; palmitic acid, 9·5; stearic acid, 5·9; oleic acid, 47·6; linolic acid, 2·9; and unsaponifiable matter 19·6 per cent. comprising 3·3 per cent. of sterols and 16·3 per cent. of squalene. A. O. J.

Determination of the Copper-content of Coffee. M. Streuli and E. Bürgin. (*Z. Unters. Lebensm.*, 1936, **72**, 531–532.)—The object of the investigation was to determine whether the use of copper vessels in the manufacture of "caffeine-free" coffee had any effect upon the copper-content of the coffee. One hundred grams of finely ground, roasted coffee were incinerated and heated with sulphuric acid until fumes were evolved, after which the residue was extracted with water and the copper was determined electrolytically by the method described by Treadwell (*Analytische Chemie*, 11th Ed., 1923, Vol. II, p. 155). The copper-content of thirteen samples of ordinary coffee varied from 1·2 to 2·4 mg. per 100 g., and that of eleven samples of caffeine-free coffee varied from 1·2 to 4·3 mg. per 100 g. When compared with the copper-content of such food material as preserved peas, spinach, tomatoes, etc., the copper-content of coffee can be regarded as negligible. Infusions were made from 100-g. portions of coffee of known copper-content by boiling with 2 litres of water and filtering the mixture while hot. The filtrate was evaporated to a convenient bulk, and the copper was determined in the infusion and in the residue. It was found that with ordinary coffee and with caffeine-free coffee, the infusion contained no copper, and that the "grounds" contained all the copper of the original coffee. A. O. J.

Stachyose in the Stalks and Roots of *Verbena officinalis* L. and in the Underground Parts of *Verbena venosa*. J. Cheymol. (*J. Pharm. Chim.*, 1937, **25**, 110–117.)—Stachyose was extracted in crystalline form from *Verbena* *officinalis* L. and from *Verbena venosa*, Gill and Hook, as follows:—An alcoholic extract of 110 g., prepared from 1250 g. of the roots, was dissolved in ten times its weight of water; the solution was defecated by lead subacetate, the precipitate was filtered off *in vacuo*, and the excess of lead was removed from the filtrate by means of sulphuric acid. The filtrate and washings were mixed in a mortar with 110 g. of powdered barium hydroxide, the mixture was filtered, and 1250 ml. of the filtrate were mixed with four times the volume of 85 per cent. alcohol. After two days the precipitated barium sugar compound was centrifuged, washed with a litre of 85 per cent. alcohol, dissolved in five times its weight of water, and decomposed with 80 ml. of sulphuric acid (10 g. per 100 ml.). After elimination of barium sulphate the excess of acid was neutralised with calcium carbonate, and the filtered liquid was distilled under reduced pressure. The extract thus obtained was taken up successively with 95, 90, and 85 per cent. alcohol. The extract was mixed with 27 ml. of water, and 140 ml. of 95 per cent. alcohol were added in small portions through the condenser to the solution obtained on warming. Stachyose crystallised from the alcoholic solutions, especially from the last one. Finally, 29·60 g. of crystals were collected, and, on re-crystallisation from 85 per cent. alcohol, these yielded 24 g. of pure stachyose. Stachyose was similarly obtained from stalks deprived of leaves and of floral stems, and from the underground portions of *Verbena venosa*, deprived of old stems. The stachyose was found to be identical with that from *Stachys tuberifera* by the following tests:—Melting-point, loss of weight on heating, rotatory power, action of invertase, and production of mucic acid. The results were characteristic of stachyose containing four mols. of water of crystallisation. E. B. D.

Detection of Ephedra Alkaloids in Small Quantities of Ephedra. J. W. Kelly. (*Amer. J. Pharm.*, 1937, **109**, 36–38.)—Two grams of the air-dried ephedra, moistened with 10 per cent. sodium carbonate solution, are thoroughly ground with a few granules of sharp sand and extracted with chloroform for an hour. An apparatus in which, during extraction, the material is warmed with the vapours of the solvent is preferable (*cf.* Butt, *J. Ind. Eng. Chem.*, 1915, **7**, 130). A simple apparatus of this type is described. The extract is shaken with 10 ml. of 10 per cent. hydrochloric acid in a 25-ml. separating funnel, and the acid solution is heated with decolorising carbon and filtered into a small test-tube. The filtrate is made strongly alkaline with 20 per cent. sodium hydroxide solution and treated with 0·1 ml. of a 2 per cent. copper sulphate solution. A blue or violet colour is given by ephedra alkaloids. If sufficiently concentrated the alkaloids may be estimated colorimetrically by comparison with a standard solution of ephedrine. If the colour is not deeper than that of the mixed reagents, the mixture is shaken with ether, and the ethereal extract is allowed to evaporate in a porcelain dish. A pink residue shows the presence of ephedra alkaloids. Very small quantities of the alkaloid can thus be detected in 2 g. of the drug. When larger proportions of the alkaloids are present, positive results are obtained with much less than 2 g. of the drug; for example, 0·2 g. was sufficient with a drug containing 0·37 per cent. of alkaloids. E. B. D.

Biochemical

Simplified Peroxidase Reaction. A. G. Douglas — S. (*Chem. Ztg.*, 1937, **61**, 130.)—The oxidase reaction of Hirschfeld (*Klin. Woch.*, 1935, **14**, 1437–8) is not ideal when repetition work is necessary. The peroxidase reaction of Graham (*Lehrb. Blutkrankh.*, 1928, **2**, 55) has been modified, and even in inexperienced hands is claimed to give excellent results. The fixation, peroxidase reaction and contrast staining can all be carried out within 3 minutes. The air-dried blood film is covered with several drops of solution I, and, after 20 to 30 seconds, an equal number of drops of solution II are added. At the end of 2 or 3 minutes the liquid is poured from the microscope slide, which is washed with several drops of solution III. The preparation is dried as quickly as possible by gently waving the slide in the air, and examined with an oil-immersion lens. The myeloid elements show brown granulations and a coloured nucleus, the colour of which depends on the stain used. A large proportion of the mononuclear cells also give a positive reaction. Solution I is prepared by dissolving benzidine (the base, not one of its salts) in dioxan until a saturated solution is obtained. This is then diluted to ten times its volume with dioxan. Solution II is made by mixing 10 ml. of a 0·5 per cent. aqueous solution of safranin with 0·1 ml. of a 3 per cent. solution of hydrogen peroxide. Dyestuffs of other colours, such as blue, may be used instead of safranin, but the nucleus will then be stained by the dye used and will not be red. Solution III is dioxan itself. All the solutions keep well.

S. G. S.

Adrenaline-content and Physiological Activity of Suprarenal Gland Extracts. H. G. Rees. (*Quart. J. Pharm.*, 1936, **9**, 659–668.)—The following modification of Folin's method for the estimation of adrenaline is recommended:—The adrenaline solution was made up to a strength of approximately 0·04 per cent. in dilute hydrochloric acid (0·2 to 0·5 ml. of conc. acid in 250 ml. of boiled distilled water). One ml. of this solution was mixed in a 100-ml. flask with 2 ml. of Folin and Trimble's reagent, followed by 5 ml. of 5 per cent. sodium hydroxide solution. After 3 minutes the mixture was diluted to 100 ml., and the blue colour was read in a Lovibond tintometer, a 1-cm. glass cell being used. The interference of ascorbic acid was overcome by determining the amount present by means of the 2:6-dichlorophenolindophenol titration. The blue value corresponding to this was then determined on a sample of standard orange juice, and when this value was subtracted from the total blue value of the sample the true adrenaline-content was obtained. If the persulphate method was used, it was found that more reliable results were obtained when the *p*H of the adrenaline solution was adjusted to 3·6–4·0. An aliquot part of the solution was taken, diluted to 4 ml. with the reagent, and incubated at 37° C. until the maximum red (Lovibond) colour was obtained. With pure solutions of adrenaline the maximum colour was obtained after 10 to 15 minutes, but with gland extracts 90 to 120 minutes were required. The adrenaline-content of desiccated, frozen or fresh suprarenal glands, as estimated colorimetrically, agreed with the value found by physiological assay. These methods of assay provided no evidence of the existence of any highly physiologically active substance similar to adrenaline in suprarenal extracts, even after careful extraction designed to prevent post-mortem decomposition. S. G. S.

Enzymic Action of Ascorbic Acid (Vitamin *C*). G. Woker and J. Antener. (*Helv. Chim. Acta*, 1937, **20**, 144–150.)—Titration with a solution of methylene blue may be used for the determination of the ascorbic acid-content of raw milk and for that of Schardinger's enzyme (and others). From a consideration of the ascorbic-dehydroascorbic acid system and other similar oxidation-reduction systems, the authors conclude that Schardinger's enzyme is identical with the ascorbic acid present in raw milk. They find further confirmation of this when the ascorbic acid redox system is compared with peroxidase systems as capillarisation fields on filter-paper, and with diastase. Further work on the enzymic properties of ascorbic acid is in progress. S. G. S.

Colorimetric Determination of Free and Combined Cholesterol. R. M. Smith and A. Marble. (*J. Biol. Chem.*, 1937, **117**, 673–684.)—The investigation was carried out on oxalated blood samples and the plasma lipids were extracted with alcohol-ether (3 : 1) as recommended by Bloor. Total cholesterol was determined on one aliquot of filtrate following Bloor's procedure (*J. Biol. Chem.*, 1928, **77**, 53). Ester and free cholesterol were determined on a second aliquot portion, the former by a method similar to that of Bloor and Knudson with the addition of saponification, and the latter by a new method. Ten or 15 ml. of the alcohol-ether filtrate are evaporated to dryness at a temperature below 60° C., and the dry residue is extracted with two 1·5-ml. and two 1-ml. portions of acetone-alcohol, filtering through a small plug of fat-free cotton-wool. Two ml. of digitonin solution (Hoffmann–La Roche 0·2 per cent. aqueous solution purified and prepared according to Schoenheimer and Sperry, *J. Biol. Chem.*, 1934, **106**, 745) are added, the liquids mixed by rotation and left to stand at least 4 hours. The liquid is then rapidly evaporated to complete dryness on a steam-bath and the ester extracted with warm petroleum spirit as in the Bloor–Knudson method (*J. Biol. Chem.*, 1916, **27**, 107), taking care that the larger part of the precipitate remains in the beaker and that none is lost. The precipitate is set aside for determination of the free fraction. Three drops of 40 per cent. potassium hydroxide solution are added to the petroleum spirit extract and saponification carried out at 75–85° C. Evaporation of the spirit, with the appearance of the characteristic syrupy saponified residue, usually takes 15–20 minutes, and the determination then proceeds as for total cholesterol. The free cholesterol is determined by adding 1 ml. of hot glacial acetic acid, drop by drop, through the funnel into the beaker containing the dry cholesterol digitonide precipitate. The beaker is warmed to complete solution and the acetic acid solution is transferred to a round-bottom 15-ml. centrifuge or culture tube, two portions of 0·5 ml. of acetic acid being used for washing out the beaker. The tube is fitted with a cork stopper, with a water-pump connection and a groove through which a stirring rod is inserted. It is heated on a sand-bath at 150–160° C., and by gentle suction the acetic acid is evaporated almost to dryness without charring. When a trace of acid remains, but before evaporation is complete, 5 ml. of petroleum spirit are added and vigorous stirring is carried out while the spirit boils. The free digitonin forms a white or yellowish precipitate and the free cholesterol passes into the spirit, which after centrifuging, is decanted into a 50-ml. Erlenmeyer flask. The digitonin precipitate is washed twice with 2 to 3-ml. portions of warm petroleum spirit and the washings are added to the original extract. The free cholesterol is determined in the spirit solution as in the total ester determination. Recovery of total cholesterol from solutions containing known amounts of free cholesterol and cholesterol acetate was found to be complete. Sperry's normal ratio of free and ester cholesterol to total cholesterol was confirmed. The factor responsible for the higher total cholesterol values usually obtained on unsaponified blood filtrates is regarded as probably associated with the ester fraction. D. G. H.

Factors Affecting the Vitamin *C* Content of Apples. E. L. Batchelder and E. L. Overholser. (*J. Agric. Res.*, 1936, **53**, 547–551.)—The factors studied were (*a*) the ratio of leaf area to fruit; (*b*) the size of fruit as it affected the ratio of skin to pulp; and (*c*) storage at 32° F. and 40° F. for 6 months. The ratio of leaf area to fruit affected the vitamin *C* content only as it affected the size of the fruit produced. The size of the fruit was important, because the ratio of skin to pulp was higher in small apples than in large ones and the skin contained more vitamin *C* than the pulp. Storage at 40° F. resulted in a greater loss of vitamin *C* than at 32° F. The tests were made on guinea-pigs, and the results quoted are for the amounts necessary for complete protection. S. G. S.

Bacteriological

Duck Salmonellosis and its Importance for Man. J. Jansen. (*A. van Leeuwenhoek Nederl. Tydschr. Hyg. Microbiol. en Serol.*, 1936, [v], **3**, 184–237; *Bull. Hyg.*, 1937, **12**, 139.)—The infection of ducks' eggs by salmonella has frequently been recorded (*cf.* ANALYST, 1933, **58**, 759) and salmonella poisoning is also of importance to the poultry farmer and the fox farmer. The two salmonella types mainly concerned are *S. typhi-murium* (= *B. aertrycke*) and *S. enteritidis* var. *Essen*, the latter being the more important. *S. enteritidis* var. *Dublin* is the chief infective agent for the silver fox; *S. anatum* is not known in Europe. Salmonella infection in ducks is chiefly known by its consequences. The chronically infected duck may develop ovaritis, the ovarian follicle, which afterwards becomes the yolk, may infect the egg and, as a result, the embryo or the young chicken may die. *S. pullorum* also infects poultry, and this organism possesses a common somatic antigen with *S. enteritidis* var. *Essen*. This antigen can be used with great advantage in the diagnosis of salmonella infections in ducks, for when the rapid serum method or the drop blood method is employed, the formolised *S. pullorum* antigen does not bring about agglutination of the erythrocytes, whereas the formolised *S. enteritidis* antigen does. Duck eggs are not much eaten in Holland, but are largely exported. So long as farms are not salmonella-free and so long as raw or imperfectly cooked eggs are consumed, as they often are in confectionery, duck salmonellosis constitutes a danger to man. D. R. W.

Rates of Fermentation of Sugars by Different Yeasts. R. de Smedt. (*Woch. Brau.*, 1937, **54**, 32; *J. Inst. Brewing*, 1937, **43**, 127.)—Different types of yeast exhibit varying capacity for the fermentation of cane sugar and maltose. The brewing yeasts (or grain yeasts) ferment these sugars about equally well, but the bakers' yeasts (or pressed yeasts) ferment maltose more slowly, particularly after long propagation in molasses worts. Experimentally, the rate of fermentation was measured by the author by the determination of the amount of alcohol produced in 3 and 6 hours at 27° C. The age of yeast has a marked influence on the fermentative activity, but it is shown that storing in closed containers at 2° to 3° C. has little effect on the activity of pressed yeast in 10 to 15 days. The decline of capacity for fermenting maltose is very marked with grain yeast, but is not so marked in pressed yeast, the initial capacity being only slight. The yeasts tested included commercial pressed yeasts, top-fermentation and bottom-fermentation yeast and *Torulopsis dattila*. D. R. W.

Cold Sterilisation of Nutrient Media and its Significance for the Pure Culture of Micro-organisms. G. Schweizer. (*Woch. Brau.*, 1937, **54**, 24; *J. Inst. Brewing*, 1937, **43**, 127.)—Sterilisation by heat alters some nutrient media and impairs their nutrient value for certain micro-organisms. The author claims that this difficulty can be overcome by the method of sterilisation at ordinary temperature which he suggests, *viz.* the treatment of the media with gaseous disinfectants in the almost complete absence of oxygen *in vacuo*. Under these conditions relatively harmless substances, *e.g.* ammonia, become actively germicidal. After sterilisation the substance used as the germicide is removed by aspirating through the medium air previously sterilised by passing through a sterile filter of cotton-wool. Obviously, only such volatile substances as have no chemical action on the medium must be used. Details of the process are deferred to a later paper. The *Wochenschrift* abstractor, Koch, expresses doubt about the effectiveness of this method for the destruction of resistant spores in media. D. R. W.

Relation between the Staining Properties of Bacteria and their Reaction towards Hop Antiseptic. J. M. Skimwell. (*J. Inst. Brewing*, 1937, **43**, 111–118.)—Recent studies of two species of beer bacteria by the author (*J. Inst. Brewing*, 1936, **42**, 119, 585) have shown that certain species of bacteria are comparatively indifferent to the antiseptic action of hops, and more recently it has been found that this indifference is shared by other species of bacteria—*Acetobacter capsulatum*, *Flavo-bacterium proteus* and *Escherichia coli*. Comparison of the characteristics of these species and of the species known to be sensitive to hops has shown that the former are largely gram-negative, whilst the latter are gram-positive. This might be only coincidence, but, in view of the selective action of crystal violet and similar dyes to gram-positive and gram-negative bacteria, it was considered worthy of investigation.

A number of species of saprophytic bacteria, obtained from the National Collection of Type Cultures, were investigated. Beer wort of sp.gr. 1·042 with a hop rate of 0·5 per cent. (1·8 lb. per barrel) was used, this rather high rate being employed in case laboratory extraction should be less efficient than that of the brewery. The *p*H was adjusted to 5·18, and the various cultures were incubated at 20° and 30° C. In every instance, without exception, the gram-negative bacteria began to grow as rapidly in the hopped as in the unhopped wort, whilst the gram-positive species were either totally or partially inhibited by the presence of hop extractives. Tables are given showing the species of bacteria tested and the growth or absence of growth in hopped wort.

Suggested relationship between the molecular structure of humulone and lupulone and their specificity towards gram-positive bacteria.—According to McCulloch's summary in "Disinfection and Sterilisation" (Kimpton): (*a*) Introduction of aliphatic or aromatic groups into the nucleus of halogen phenols increases the bactericidal potency (up to a certain limit), this increase depending, in the case of alkyl substitution, upon the number of carbon atoms in the substituting group or groups; (*b*) the effect is greater with a normal chain than with a branched chain; (*c*) a quasi-specific germicidal action is shown with the higher homologues, in that with further increase in weight of the substituting group the germicidal capacity drops to almost zero with certain bacteria, but rises to great heights with others. On these principles an explanation for the specific antiseptic properties of humulon and lupulone is suggested, and the greater toxicity of lupulone towards *Lactobacillus bulgaricus* is tentatively ascribed to its possessing an additional substituting aliphatic chain. D. R. W.

Toxicological

Post-mortem Study of the Alleged Transformation of Barbituric Derivatives into Hydrocyanic Compounds. P. R. Orella. (*Rev. Fac. Cienc. Quim.*, 1935, **10**, 51–60.)—In an attempt to confirm the statement of Kohn-Abrest, that hydrocyanic acid is always found either combined or, more rarely, in the free state in the decomposed viscera of those who have died as a result of poisoning with barbituric compounds, such as veronal, gardenal and dial, the author carried out a series of experiments on four dogs. One was killed by strangulation, and the other three were poisoned by the oral administration of 5 g. of veronal, luminal and prominal, respectively, and strangled one hour after the dose was given. The blood and viscera were used for examination. On the day after death the chest and abdominal viscera were examined for free hydrocyanic acid by distillation in presence of phosphoric acid, and for combined hydrocyanic acid by distilling the residue from the first distillation with potassium chromate solution and sulphuric acid; one-eighth of the weight of each organ was used for the analysis. On the 8th, 30th and 60th days the analyses were repeated, one-eighth of the weight of each organ again being used. Neither in the poisoned dogs nor in the one killed without administration of poison was any trace of free or combined hydrocyanic acid found, so that the hypothesis of Kohn-Abrest was not confirmed. It is suggested that the thiocyanate in the saliva of smokers and of those who are in the habit of eating large quantities of condiments, such as mustard, may have led previous workers to the conclusion that the presence of hydrocyanogen compounds was a result of ingestion of barbituric derivatives. Tables of the author's results are given in detail. E. M. P.

Organic

Determination of Iodine in Organic Substances. J. A. Gautier. (*J. Pharm. Chim.*, 1937, **25**, 145–155.)—Ten ml. of *N* sodium hydroxide solution and 1 g. of zinc powder are added to the substance (2 to 20 cg. depending on the iodine-content), contained in a conical flask. The liquid is boiled for 15 to 30 minutes, when conversion of the combined iodine into sodium or zinc iodide should be complete. For substances insoluble in sodium hydroxide solution, *N* alcoholic potash should be used, and the flask heated under a reflux condenser. After cooling, the liquid is diluted to 50 ml., and 10 ml. of *N* sulphuric acid are added. This results in precipitation of zinc hydroxide, which is filtered off after dilution of the liquid to a known volume. To an aliquot part of the filtrate, 5 ml. of *N* sodium hydroxide solution and 10 to 20 ml. of saturated potassium permanganate solution are added, and the liquid is boiled for 10 minutes (if alcoholic potash has been used, the alcohol must be removed by distillation prior to adding the permanganate). The excess of permanganate is then destroyed by the addition of sufficient alcohol to the hot liquid, and the brown manganese hydroxide precipitate is filtered off after dilution of the liquid to a known volume. An aliquot part of the filtrate is boiled with 1 g. of ammonium chloride and 10 ml. of glacial acetic acid to eliminate nitrite. The cooled acid liquid, which contains the iodine as iodic acid, is treated with 1 to 2 g. of potassium iodide, and, after it has stood in a dark place for 5 minutes, the liberated iodine is titrated. Good results were obtained with a number of organic iodine compounds, *e.g.* thyroxin. The method is not applicable to very volatile compounds, such as iodomethane, or to insoluble compounds, such as aristol. Two compounds, *viz.* iodol and uroselectan, yielded somewhat low results. S. G. C.

Preparation of Pure Oleic Acid by a Simplified Method. J. B. Brown and G. Y. Shinwara. (*J. Amer. Chem. Soc.*, 1937, **59**, 6–8.)—Oleic acid may be prepared from olive oil by first separating the saturated fatty acids by precipitation from acetone solution at −20° C., and then crystallising the unsaturated fatty acids from acetone at −60° C. at least four times, followed by a partial crystallisation from acetone at −35° C. to remove any palmitic acid not removed by the original crystallisation at −20° C. Three samples were prepared by this method, and by slight modifications of the method, and these had the following constants:—m.p., 13·0, 13·0, 13·0° C.; mean molecular equiv., 282·2, 282·4 and 282·5; iodine value, 90·03, 89·63, and 90·04; n_D^{20}, 1·4585, 1·4586 and 1·4585. D. G. H.

Quantitative Determination of Furfural and Hydroxymethylfurfuraldehyde with *p*-Nitrophenylhydrazine. L. Maaskant. (*Rec. Trav. Chim. Pays-Bas*, 1936, **55**, 1068–1070.)—For the investigation of the quantitative determination of furfural with *p*-nitrophenylhydrazine according to the method of van Ekenstein and Blanksma (*Rec. Trav. Chim. Pays-Bas*, 1903, **22**, 434; 1905, **24**, 33; *Chem. Weekblad*, 1909, **6**, 219) 0·4190 g. of furfural (b.p. 160·5° C.) was dissolved in water and the solution was made up to 100 ml. Ten-ml. portions of the solution were treated with twice the theoretical quantity of *p*-nitrophenylhydrazine in 30 per cent. acetic acid; the latter solution was prepared by adding 0·7 g. of *p*-nitrophenylhydrazine to 50 ml. of 30 per cent. acetic acid, heating the liquid to boiling, allowing it to cool, and filtering from insoluble matter. The liquid containing the furfural and *p*-nitrophenylhydrazine was heated to boiling and left until the following day, when the precipitate was collected on two counterpoised filter-papers folded one inside the other, washed with water, and dried at 105° C. to constant weight. The m.p. of the furfuraldehyde *p*-nitrophenylhydrazone was 154° C. Similar experiments were carried out with 0·3696 g. of pure hydroxymethylfurfuraldehyde (m.p. 32° C.), which yielded a *p*-nitrophenylhydrazone melting at 183° C. The results of the determinations are given in the table.

p-Nitrophenylhydrazone of	Weight of precipitate g.	Furfural or hydroxymethylfurfuraldehyde	
		Calculated g.	Theoretical g.
Furfuraldehyde	0·1000	0·0416	0·0419
,, ,, ...	0·0994	0·0413	
Hydroxymethylfurfuraldehyde	0·0764	0·0369	0·0370
,, ,,	0·0758	0·0366	

It is concluded that *p*-nitrophenylhydrazine is a more satisfactory reagent than phloroglucinol (experiments with which are quoted), as the precipitate obtained is a compound with a definite melting-point; also, phloroglucinol cannot be used for the determination of less than about 9 mg. of hydroxymethylfurfuraldehyde. In addition, in the determination of pentosans the formic acid produced by boiling hydroxymethylfurfuraldehyde for 2 to 3 hours with 12 per cent. hydrochloric acid gives a precipitate with phloroglucinol and hydrochloric acid, so that the use of *p*-nitrophenylhydrazine is preferable. E. M. P.

Purification of Linolic Acid by Crystallisation Methods. J. B. Brown and G. G. Stoner. (*J. Amer. Chem. Soc.*, 1937, **59**, 3–6.)—The preparation of linolic acid without bromination was carried out by direct crystallisation, cottonseed and maize oils being used as sources. The saturated and unsaturated fatty acids were separated by crystallisation at −20° C. from a 10 per cent. solution in acetone. The unsaturated acids then contained about 70 per cent. of linolic acid, and further crystallisation of the acids, and especially of their methyl esters, from acetone or methyl alcohol at temperatures between −40° and −80° C. yielded linolic acid of purity up to 93 per cent. Lithium soaps prepared from the fatty acids and crystallised from *n*-butyl alcohol, and potassium soaps crystallised from absolute alcohol, also gave useful linolic acid concentrates. D. G. H.

Reactions of Mustard Gas. H. L. Ligtenberg. (*Pharm. Weekblad*, 1937, **74**, 185–197.)—Existing reactions are critically reviewed, and may be classified as follows:—(1) *Specific Reactions.*—Grignard, Rivat and Scatchard's test (*Ann. de Chim.*, 1921, **15**, 5), which depends on the formation of phenyl carbamine chloride by the action of sodium iodide, in the presence of copper sulphate as a catalyst, is sensitive only if the sample is warmed and if the concentration is relatively high (*e.g.* 30 g. per cb.m.). The gold chloride test, in which a yellow addition-product is formed (Schröter, *Z. angew. Chem.*, 1936, **46**, 164), can be made sensitive to 4 g. per cb.m. by the following procedure:—One drop of a 0·1 per cent. solution of the reagent is placed in the constricted bend of a U-tube, one arm of which is blown into a bulb, in such a way that air drawn through the tube bubbles through the liquid; for transport purposes the ends of the tube are closed with short lengths of rubber tubing in which are inserted glass rods. The arm containing the bulb is connected with a 250-ml. suction-pump, the other arm being connected, through a dust-filter, with a metal funnel 10 cm. in diameter, and this is placed over the area on the ground which it is desired to examine. In this way the contaminated air may be drawn through the reagent, the first appearance of turbidity being most easily observed against a dark background, or, at night-time, by means of a blue light. *Sensitive but non-specific reactions.*—These usually depend on reduction reactions. In the Yablick, Perrot and Furman test (*cf.* ANALYST, 1920, 45, 146) 0·05 ml. of a 1 per cent. solution of selenic acid in 50 per cent. sulphuric acid was reduced after 10 minutes at 85° C. in the presence of 0·012 mg. of mustard gas. This reaction, however, is somewhat inconvenient, and is also sensitive to carbon monoxide or sulphur dioxide; 1 drop of a 0·0035 per cent. solution of potassium permanganate, which turns brown on reduction, is preferred. The special value of this test is that if it is negative it is safe to assume that mustard gas or arsine is absent. A solution of methyl orange in water is turned red by mustard gas in 4 minutes, owing to the formation of hydrochloric acid by hydrolysis, but diphosgene also produces this change, although more rapidly. Paper which has been lightly coloured with Sudan red (preferably by soaking it in a solution of the dye in petroleum spirit) develops a blood-red colour with mustard gas, but also with other vapours, *e.g.* those of petroleum, benzol, chloropicrin and alcohols, and with fatty substances. A preferable procedure, which increases the sensitiveness of the reaction, is to distribute the particles of dye in a porous white medium through which the mustard gas can penetrate. J. G.

New Apparatus and Method for Determining the Water-absorption Capacity of Leather. V. Kubelka and V. Nemec. (*J. Intern. Soc. Leather Trades Chem.*, 1937, 21, 9–12.)—A cylindrical vessel of chromium-plated brass (40 mm. high and 80 mm. in diameter) roughened on the outside, is screwed into an upper conical portion having a brass tube, 35 mm. long and 10 mm. in diameter, at the narrow end. On the sloping inner surface of the cone is fixed a small piece of metal (to prevent the leather from lodging on the surface), and opposite this is a small hole which acts as a valve for pressure-changes which may occur as the result of variations in the temperature of the room. By means of a connecting collar provided with a fine thread, a glass flask with a long neck, having a total capacity of 75 ml. at 20° C., is connected with the narrow brass tube. The neck is calibrated from 0 to 15 ml. in 0·1 ml. intervals, and the calibrations start from what would normally be the top of the neck. All grease is removed from the apparatus by suitable cleansing agents, and a blank test is made by filling the flask with 75 ml. of distilled water, attaching it to the brass tube, and allowing the water to run into the metal cylinder (care being taken that none escapes through the small hole). After a few minutes the apparatus is re-inverted (so that the flask is again at the bottom), and the water-level is read after 10 minutes; the wetting-error, which should not exceed 0·3 ml., is used as a correction. This procedure is repeated with a weighed circular piece of leather (70 mm. in diameter and having a moisture-content of 17 per cent.) in the metal vessel, but the readings are taken after the leather has been in contact with the water for 30 minutes and 24 hours at 20° C., 10 minutes being allowed for drainage after inverting the apparatus each time. If K_g is the weight of leather and P ml. the reading (*i.e.* water absorbed), then the water-absorption capacity after any particular period is given by 100 P/K. It is important to make at least two measurements, in order to distinguish between capillary absorption, which increases rapidly with time, and molecular absorption which is a much slower process, and is probably accompanied by swelling of the leather fibres. These effects are demonstrated by the time-absorption curves given by five Czechoslovakian leathers; these show a rapid initial absorbency, which increases very slowly or remains constant after 4 to 8 hours. The absorption-capacity depends on the degree of tannage. Thus, dried pelt (moisture-content 16 per cent.) swells rapidly and absorbs 200 to 300 per cent. of water, whilst leather tanned to the extent of only 30 per cent. of its thickness absorbs a great deal of water, but reaches the point of maximum swelling in a few minutes and thereafter absorbs no more. Leathers which are completely tanned (*e.g.* by the old pit method) but contain no excess of tanning materials, give similar curves, because the pores are empty, whilst if one of the modern types of tanning process (involving the deposition of tannins in the structure of the leather) has been used, maximum absorption is attained after a longer period, as the deposited tannin is dissolved out only gradually. J. G.

Inorganic

Colorimetric Determination of Silver as Colloidal Silver Sulphide. L. de Brouckère and R. Petit. (*Bull. Soc. Chim. belg.*, 1936, 45, 717–725.)—Saturated hydrogen sulphide water (2·5 ml.) was introduced into each of two colorimeter glasses. The silver solution to be tested (25 ml.), acidified with nitric acid and containing 0·04 g. per litre of gelatin as protective colloid, was put into one glass, and the same volume of standard silver solution containing the same amount of acid and gelatin was put into the other. It was found necessary to make the additions simultaneously and at the same rate, with the aid of two burettes operated one with each hand. The silver sulphide suspensions were compared in a Duboscq colorimeter. Results within about 2 per cent. of the theoretical were obtained if the following conditions were satisfied: (*a*) the concentration of silver in the test solution was between 5×10^{-6} and 5×10^{-4} g.-atom. of silver per litre (0·00014 and 0·0014 g. of silver in 25 ml.); with lower concentrations it was found difficult to match the colours, and with higher concentrations the silver sulphide tended to flocculate; (*b*) the acidity was between 0·03 and 0·13 N in nitric acid, preferably 0·1 N; (*c*) the standard silver solution was of similar strength to the test-solution (less than 100 per cent. difference in strength). S. G. C.

Reducing Action of Mercury: Hydrogen Peroxide Formation and Catalytic Action of Copper in the Reduction of Molybdenum. W. M. Murray and N. H. Furman. (*J. Amer. Chem. Soc.*, 1936, 58, 1843–1847.)—

It is known that when mercury and dilute hydrochloric acid are shaken together in presence of air, some hydrogen peroxide is formed. Mercury can nevertheless be used for the quantitative reduction of, *e.g.* ferric, vanadic and molybdic ions. The suggested explanation is that the reduced metal ions readily catalyse the decomposition of the hydrogen peroxide, destroying it as fast as it is formed. If, however, only small quantities of these metals are present, the mercury reduction is not reliable unless oxygen is excluded. Also, in the determination of even large amounts of antimony, oxygen must be excluded, because the hydrogen peroxide is not decomposed catalytically by the antimonite formed. In the presence of small amounts of copper the mercury reduction of molybdic ions was found to be incomplete in the presence of air. The reason found for this was that the quinquevalent molybdenum first formed is rapidly autoxidised by copper in the presence of the hydrogen peroxide formed, according to the following sequence of reactions:—

(1) $Cu^{II} + Mo^{V} \rightarrow Cu^{I} + Mo^{VI}$.
(2) $2H^{\cdot} + 2Cu^{I} + O_2 \rightarrow 2Cu^{II} + H_2O_2$.
(3) $2H^{\cdot} + 2Mo^{V} + H_2O_2 \rightarrow 2Mo^{VI} + 2H_2O$.

S. G. C.

Apomorphine as Indicator in the Bromate Titration of Antimony. L. Szebellédy and K. Sik. (*Z. anal. Chem.*, 1937, **108**, 81–85.)—Apomorphine hydrochloride solution gives with free bromine a vivid rose-red colour, which is discharged by tartar emetic. The base acts as a reversible oxidation-reduction indicator. The antimony solution (50 ml.) should contain not more than 5 per cent. of free hydrochloric acid. It is treated with 0·3 ml. of a 0·1 per cent. solution of apomorphine hydrochloride in 5 per cent. hydrochloric acid, warmed to 45 to 50° C., and titrated with 0·1 N bromate solution until the last drop gives a rose-red end-point. Near the end-point, 10 to 20 seconds should be allowed to elapse after the addition of each drop of standard solution. The procedure furnishes proportional results, no correction for the bromine consumed by the above quantity of indicator being necessary; 0·6 ml. of indicator requires a correction of 0·05 ml. of bromate solution.

W. R. S.

Spot-test for the Detection of Osmium. N. A. Tananaeff and A. N. Romanjuk. (*Z. anal. Chem.*, 1937, **108**, 30–32.)—A drop of the solution to be tested is placed on filter-paper and treated with a drop of a saturated solution of benzidine in acetic acid. Traces of osmium tetroxide give a blue colour which gradually turns violet. A similar test may be carried out with a solution of potassium ferrocyanide in acetic acid, which gives a light-green colour. The sensitiveness of both tests is 10γ of osmium in 0·001 ml.; it is increased if the unknown solution is boiled in a test-tube provided with a perforated stopper through which passes a short glass tube terminating in a jet. The steam is made to impinge on the drop of benzidine solution on the filter-paper, the colour then appearing within half-a-minute. The distillation test is more reliable, as ruthenium, silver and gold react with benzidine in the same way as osmium.

W. R. S.

New Colour Test for Magnesium. E. Eegriwe. (*Z. anal. Chem.*, 1937, **108**, 34–37.)—Benzoazurin G (dye No. 497 of Schultz-Lehmann's *Farbstofftabellen*, 7th Edition) turns pink on treatment with ammonia and yields a violet-blue to blue lake with magnesium hydroxide. One drop of the solution to be tested, which should be neutral to litmus and free from ammonium salt, is treated with 1 or 2 drops of 0·1 per cent. aqueous solution of the dye and several drops of strong ammonia solution. A blue colour is obtained with 0·5γ of magnesium at a concentration of 1:90,000. Large quantities of magnesium give a violet-blue precipitate. The reaction is specific for magnesium, but copper, nickel and cobalt interfere, as they react with ammonia. Metals other than lead, cadmium, zinc, alkaline-earth and alkali metals, should not be present. W. R. S.

Determination of Magnesia in presence of Zinc by means of Oxine. S. J. Fainberg and L. H. Fligelman. (*Zavodskaya Laboratoriya*, 1936, No. 8, 942–945.)—Precipitation of zinc by oxine (8-hydroxyquinoline) can be prevented by converting it into complex cyanide (*cf.* Heczko, ANALYST, 1935, **60**, 120). The tervalent metals, together with lead, are precipitated with ammonia, and calcium is precipitated with sodium oxalate. Copper does not interfere. The filtrate, after removal of tervalent metals and calcium, is placed in a conical 500-ml. flask, 5 ml. of 25 per cent. sodium sulphite solution are added to prevent the formation of ferricyanide from traces of iron, followed by 10 ml. of 30 per cent. sodium hydroxide solution and 23 ml. of 30 per cent. potassium cyanide solution. The liquid is diluted to about 300 ml. and heated on the water-bath to 60°–70° C., 7 to 10 ml. of a 1·5 per cent. solution of oxine in acetic acid are added, with stirring, and the mixture is heated on a water-bath for 25 to 30 minutes, with frequent stirring, filtered through a rapid filter-paper and the precipitate washed 5 or 6 times with hot 1 per cent. sodium hydroxide solution. The precipitate is washed back into the flask with water, and the filter is washed with 25 ml. of hydrochloric acid (1 : 1), the washings being also collected in the flask, which is then heated at 70 to 80° C. The flask is shaken until the precipitate has dissolved, the volume is made up to 120 to 150 ml. and, after the addition of 1 or 2 drops of methyl orange, the liquid is titrated with $N/10$ potassium bromate bromide solution until the colour is discharged. One or two more drops of methyl orange are added, and the titration is continued until the fresh indicator is decolorised. The excess of bromine is titrated with thiosulphate solution. One ml. of $N/10$ bromate bromide corresponds to 0·504 mg. of MgO. S. P. S.

Catalytic Method for the Determination of Iodine. H. P. Lundgren. (*J. Amer. Chem. Soc.*, 1937, 59, 413–416.)—It has been found that the reduction and decolorisation of methylene blue by sulphite, which is very slow at an acid concentration of 2 N, is accelerated by iodide, owing to a catalytic effect, and that the rate of decolorisation of the methylene blue is proportional to the iodide concentration. On this principle has been based a colorimetric method of determining iodide, which is applicable to quantities of the order of a few micrograms. The reaction requires to be carried out under special conditions involving absence of free circulation of air above the liquid, and a suitable colorimetric cell has been designed for this purpose. For working details the original paper should be consulted. S. G. C.

Volumetric Determination of Sulphate with Barium Chloride and Sodium Rhodizonate. A. Mutschin and R. Pollak. (*Z. anal. Chem.*, 1937, **108**, 8–18.)—This is a preliminary communication, discussing earlier attempts at using rhodizonic acid derivatives as indicators in the titration of sulphate with barium chloride and the controversies over the proposed methods. The authors explain the principles of their modified procedure, which consists in slowly titrating a barium solution, containing 3 per cent. of ammonium chloride and 35 per cent. of acetone, with 0·2 *N* ammonium sulphate solution in presence of 1 ml. of freshly prepared, saturated sodium rhodizonate solution, the bluish-red liquid changing to orange-red, orange, and finally to yellow. Indirect titration for sulphate is unavoidable. An excess of 0·2 *N* barium chloride solution is added all at once, and the excess of precipitant is determined as described. A mechanical stirrer is used, and the sulphate solution is added drop by drop. Full details will be given in a subsequent paper. (*Cf.* ANALYST, 1933, **58**, 752.) W. R. S.

Microchemical

Spot Tests for Organic Compounds, X. F. Feigl and O. Frehden. (*Mikrochem.*, 1935, **18**, 272–276.)—*Detection of oxalic acid by the formation of aniline blue.*—A crystal of the substance under examination (a solution must be evaporated to dryness) is melted with a little diphenylamine in a micro-test tube heated over a free flame and the fused mass is taken up in a drop of alcohol. A blue colour indicates oxalate, whilst no colour should be produced in a blank test. The limit of identification is 5γ of oxalic acid. The following acids give no colour under the same conditions:—formic, acetic, propionic, tartaric, succinic, dihydroxymaleic, benzoic, phthalic, tricarballylic, glycollic, citric, and glyoxylic. When oxalic acid is to be detected in the presence of a number of anions precipitated by calcium chloride it is best to precipitate the calcium salts in acetic acid solution, to wash the precipitate thoroughly with water and to dry it by heating or by washing with alcohol and ether. A small amount of the precipitate is mixed with a little diphenylamine in a dry test-tube, heated over a free flame with a little syrupy phosphoric acid. Oxalic acid is liberated, with the formation of calcium phosphate, and the solution turns blue through the formation of aniline blue. The colour disappears on cooling, but when the melt is taken up in alcohol a bright blue colour appears. The dyestuff may be extracted from the aqueous solution with ether, giving a violet solution. All oxalates give this reaction, whether insoluble or not, so long as no excess of oxidising agent is present. For the detection of oxalic acid in a strongly acid solution it is advisable first to precipitate it as thorium salt and then to apply the aniline blue test to the precipitate. J. W. M.

Micro-determination of Chlorine. I. M. Korenman. (*Mikrochem.*, 1936, **19**, 144–146.)—Winkler's method (*Pharm. Zentralhalle*, 1933, **74**, 194), in which active chlorine in water is determined by decolorisation of methyl red, has been tested. The methyl red is used in 0·01 per cent. solution containing 1 ml. of

N alkali in 100 ml. of solution. One ml. of this solution should be exactly equivalent to 0·05 mg. of chlorine, but three different commercial preparations of the dye gave different values, 0·053, 0·054 and 0·057 mg. of chlorine being equivalent to 1 ml. It is therefore necessary to standardise the methyl red against a chlorine solution. The chlorine solution is acidified with hydrochloric acid, and a permanent (lasting at least 5 minutes) red colour indicates the end of the titration; the last drops of methyl red are very slowly decolorised. A blank gives the amount of methyl red necessary to impart the same colour to the same volume of pure water. The results obtained by this method and by the iodimetric method agreed well. Methyl orange (in 0·001 molar solution) is also used for the titration of chlorine, being standardised against known amounts of chlorine. Methyl red has the advantage that the decolorisation is more rapid near the end-point, and it gives equally good results. J. W. M.

Dipicrylamine as a Reagent for Potassium, Rubidium and Caesium. C. J. van Nieuwenburg and T. van der Hoek. (*Mikrochem.*, 1935, **18**, 175.)—Poluektoff first recommended dipicrylamine as a spot-test reagent (*Mikrochem.*, 1933–34, **14**, 265; Abst., ANALYST, 1934, **59**, 650). This substance is equally useful as a reagent for crystal formation. Potassium dipicrylaminate crystallises readily in large yellow rhombs or hexagons (10–100μ), showing pronounced birefringence. Even from very dilute solutions which give no visible precipitate the crystallisation is abundant and typical at the edge of the drop after some time. Crystals formed too rapidly from concentrated solutions may be re-crystallised from hot water. The limit of identification lies between 0·01γ and 0·1γ. In order to avoid contamination from the glass when testing for very small amounts, the test should be carried out on a sheet of cellophane. Ammonium, rubidium and caesium salts interfere, but sodium and lithium salts do not. As the reagent is used in a sodium carbonate solution, the alkaline earths, etc., must first be removed with sodium carbonate. Rubidium gives the same reaction, the crystals being slightly smaller but very similar to those obtained with potassium. The limit of identification is similar. Caesium gives rise to two types of crystals—one similar to the rubidium crystals and the other consisting of long fine needles forming bundles and star-like aggregates, highly birefringent with inclined extinction. The limit of identification is 0·01γ. When the test is carried out in a medium of equal parts of glycerin and water the sensitivity is less, but only the second, more characteristic, crystals form, so that 20γ of caesium may be detected in the presence of 200γ of potassium or rubidium, or 10γ of potassium or rubidium may be detected in the presence of 100γ of caesium. Five photomicrographs are given. J. W. M.

Physical Methods, Apparatus, etc.

Use of Polarised Light for the Examination of Manuscripts and Printed Books. R. B. Haselden. (*Library J.*, 1936, Dec. 1st.)—Polarised light from a Marks polarising biplate, Type E (diameter 1 1/16, and thickness 1/8 inch) may be used to eliminate the glare which masks the true colour and structure of markings due to pencil, ink, pigments or gold. The analyser, which has an aperture of 8 mm., is placed over the 6× eyepiece of an Ultropak microscope fitted with a 3·8× objective, the polariser being placed in the filter-slot in the lamp-housing. When the former is turned so that the planes of polarisation are at right angles, the desired elimination of glare is obtained, and minute details, otherwise invisible, may be observed; the specimen should then also be examined with the planes of polarisation parallel. On the other hand, striae in pencil strokes are best examined in unpolarised light with the aid of a sector-stop. The Marks biplate is colour-neutral and enables a 99·5 per cent. extinction to be obtained between 375·0 and 850·0$m\mu$. It lasts indefinitely if it is not scratched, exposed to moisture or heated above 75° C., and when a 120° cone of light is used, polarisation is equally effective at all angles of incidence; the transparency of one biplate to light is approximately 25 per cent. J. G.

Colour Response in Photography by Neon Light. J. A. M. Van Liempt and P. Leydens. (*Rec. Trav. Chim. Pays-Bas*, 1937, **56**, 26–28.)—The effects on various makes of unsensitised, orthochromatic and panchromatic plates, of the red, yellow, green and blue rays emitted by the following sources of light have been compared:—(1) North daylight from an unclouded sky. (2) Neon radiations from a Philips Plant-Irradiation lamp (type 4310, 220 volts, 475 watts; length of tube 1 m.; illumination-intensity, 6600 International Lumens). (3) A combination of the Philips mercury lamp (type No. 250, 250 watts) and the above neon source, having luminosity values of 2000 and 500 lux, respectively, as measured by the flicker photometer. The results show that, compared with daylight, the neon source gives satisfactory results with orthochromatic plates; with panchromatic plates satisfactory results are obtained for the red rays, but the sensitiveness in the blue region is lower than with daylight. Owing, however, to the blue predominating in the mercury lamp, satisfactory results were obtained in this region by using the mixed source (3). The mercury and sodium source previously described (*Phot. Korr.*, 1936, **72**, 142) is preferable for the yellow region. J. G.

Reviews

GÄRUNGSCHEMISCHES PRAKTIKUM. By K. BERNHAUER. Pp. xviii + 249.
Berlin: Julius Springer. 1936. Price RM.12.60.

It is not very many years since alcohol and acetic acid were the only products prepared on the industrial scale by fermentation. As compared with purely chemical processes, fermentation processes have certain obvious advantages, such as low temperature of operation and, in many cases, cheapness of raw material. These advantages have so stimulated research that a considerable number of substances are now produced on the large scale by fermentation processes which formerly were produced by chemical processes or not produced at all.

In the present work, after a short description of the general methods and operations of fermentation processes, Dr. Bernhauer gives a brief but comprehensive account of fermentation processes and more particularly of those of recent industrial application, of those not yet industrially applied and of some which at present appear to be of scientific interest only. These processes are classified under yeast fermentations, anaerobic and aerobic bacterial fermentations and mould fermentations.

The applications of the fermenting system, yeast—sugar, to the hydrogenation of unsaturated compounds and as a mild reducing agent are also described. One such example is particularly interesting; in presence of fermenting sugar, *m*-dinitrobenzene is reduced to *m*-nitroaniline and *m*-dinitroazoxybenzene.

The book, which merits a stronger binding, should prove useful both to those engaged in the fermentation industries and to the "pure" organic chemist.

LEWIS EYNON

A TEXT-BOOK OF INORGANIC CHEMISTRY. Edited by J. NEWTON FRIEND, D.Sc., PH.D., F.I.C. Vol. XI, Part IV: ORGANIC DERIVATIVES OF SELENIUM, TELLURIUM, CHROMIUM AND PLATINUM. By ARCHIBALD EDWIN GODDARD, M.Sc. Pp. xxviii + 291. London: Charles Griffin & Co., Ltd. 1937. Price 20s. net.

This work concludes Volume XI of Dr. Newton Friend's Text-book, and describes 1166 selenium, 489 tellurium, 90 chromium, and 8 platinum compounds; the author points out that this is the first compilation of its kind. The subject is, of course, almost wholly the result of work done during the present century, the bulk of the researches on tellurium having been carried out by Drew, Lederer, and Morgan. The preparation of organic selenium compounds is the subject of numerous German patents, most of which the reviewer consulted in order to find out the possible uses of these complex and, presumably, highly toxic substances. He ascertained that several compounds have been patented with a view to their use as dyestuffs, while the greater number are believed by the patentees to find therapeutic applications, either as such or in the form of their derivatives.

The compounds of selenium and tellurium are subdivided into aliphatic, the much more numerous aromatic, and miscellaneous, including a great variety of heterocyclic, derivatives. The chromium compounds are chiefly penta-, tetra-, and triphenyl derivatives, while the few platinum compounds belong to the trimethylplatinic type. The author had in view a detailed text-book giving full preparative directions in as many cases as possible, so as to assist investigators with no university library at their disposal. He has discharged his task with complete success, and produced a book bearing the stamp of painstaking and thorough compilation. In fact, the treatment of this remote borderland province of organic chemistry is much more elaborate than that accorded to some of the most important elements in the earlier text-books of the series, a lack of uniformity which will, it is hoped, be corrected by the re-writing of future editions of the older volumes.

A few additional pages on the quantitative analysis of the organic derivatives of selenium and tellurium would have been interesting and useful.

W. R. SCHOELLER

Coal: its Constitution and Uses. By **Wm. A. Bone**, D.Sc., Ph.D., F.R.S., and **Godfrey W. Himus**, Ph.D., M.I.Chem.E., D.I.C. With a Supplementary Chapter upon Fuel Economy and Heat Transmission in Industrial Furnaces, by **Reginald J. Sarjant**, D.Sc., D.I.C. London, New York and Toronto: Longmans, Green & Co. 1936. Price 25s. net.

In the space of an ordinary review one can do little more than indicate the nature of the contents of this monumental work, which covers 620 large octavo pages, with 11 pages of index, and contains 136 statistical tables, 27 full-page plates, and over 100 smaller figures and diagrams.

The two introductory chapters give the economic history of coal production since the war, and statistics of reserves and output, not only for Great Britain, but for the other coal-producing countries of the world, and discuss in a preliminary way the problems facing British coal-production—the contest between coal and oil, for example, and the production of oil from coal. These two chapters, reprinted as a pamphlet, would be valuable information for the ordinary citizen, and especially perhaps for those ordinary citizens who, without such information, ventilate their views on coal problems in the columns of the daily press.

We are then taken into the question of the origin and formation of coal, and an account is given of celluloses, lignins, proteins, resinous compounds, etc., and of the results of recent microscopic work on coal. The characters of peat, lignites and bituminous and anthracitic coals are given, and the possibilities of their derivation one from the other are discussed.

The extent and characters of the carboniferous coalfields of the world are given in Chapter VII, and Chapter VIII discusses the proximate and ultimate composition of coals, with brief references to the ordinary methods of coal analysis.

The next three chapters are devoted to the constitution of coal, and the results are discussed which have been obtained by carbonising coal, by the action of solvents upon it, and by its wet oxidation by permanganate. The essentially benzenoid character of the coal-substance, and the increased proportion of benzene-carboxylic acids derivable from it as we travel from lignite to anthracite, are insisted on.

There follows a chapter on spontaneous oxidation and weathering, embodying the results of many researches, from Richter in 1868 onwards. The conclusion is reached that pyrites can play but a very small part in the oxidation and heating of coal, and that oxidation probably begins by the direct absorption of oxygen to form loose "complexes," which afterwards decompose with production of carbon dioxide and water, and evolution of heat. Connected with this is the combustion of coal, and discussion of the relations between the two oxides of carbon at different temperatures. Judgment is suspended on this matter; it is suggested that Baker's view of the initial formation of carbon monoxide, when solid carbon burns, has much to support it, though Rhead's idea that a complex C_xO_y is first produced and afterwards decomposes with evolution of both gases cannot be dismissed.

The actions taking place in the fuel-bed of a furnace are discussed at some length, and the importance of properly arranging the secondary air supply is emphasised.

Chapter XIV is devoted to the question of the smoke nuisance, which is very fully discussed, as to its origin, its effects, and its diminution or removal. An account is also given of the recent work on the removal of sulphur compounds from flue gases, as carried out at the Fulham and Battersea power stations. Then follows a short chapter on smokeless fuels, solid, liquid, and gaseous.

On what may be called the industrial side of the book there are chapters on the cleaning of coal and its preparation for the market, on the management of coal-fired steam boilers, on pulverised and colloidal fuels, on the gas industry, the coke-oven industry, the production of semi-coke by low temperature carbonisation, water gas and producer gas, fuel economy in the iron and steel industry, and in the working of reciprocating engines and turbines, and on domestic heating. The book ends with chapters on the production of oil by hydrogenation of coal, on surface combustion and the Bonecourt boilers and furnaces, and with an elaborate monograph on fuel economy and heat transmission in industrial furnaces by Dr. R. J. Sarjant.

As was to be expected from its authorship, the work is thorough, and the exposition is throughout clear. Opened at any place at random, reading is easy and pleasant, although (perhaps because) there is no periphrasis or superfluous verbiage. In compressing into a single volume such an array of different aspects of the subject, omissions were doubtless inevitable, but as far as the present reviewer has seen, such omissions are few; and the inquirer into any one of the subjects treated in the book will almost certainly, either there or with the help of the short bibliographies at the ends of the chapters, find all that is as yet known about it. Moreover, on disputable questions, Professor Bone, doughty champion of his own views though he be, has given the views of others with the utmost fairness, and has voted for suspension of judgment wherever there was reasonable doubt.

No one whose work touches coal from any aspect can afford to be without this book; and it will be read not only with profit, but with pleasure.

J. T. DUNN

LABORATORY MANUAL FOR CHEMICAL AND BACTERIAL ANALYSIS OF WATER AND SEWAGE. By FRANK R. THEROUX, EDWARD F. ELDRIDGE, M.S., and W. LEROY MALLMANN, Ph.D. Pp. xi + 228. New York and London: McGraw-Hill Book Company, Inc. 1936. Price 15s. net.

The first edition of this book was a rather curious production, being litho-printed typescript. Despite its singularly irritating format it was accorded, so the authors tell us, a wonderful reception. In this second edition, which follows after an interval of only twenty months, normalcy has been attained, and typographically the work reflects credit on the publishers. The last named in the tripartite authorship is a newcomer who, presumably, has provided the bacteriological section which has now been added. The Manual deals mainly with the chemical aspect, and appears to be addressed primarily to those who are not skilled analysts but have to use and examine the materials concerned.

The first chapter is a collection of the analytical methods employed in the examination of water and materials used for water treatment; no indication is given where the former end and the latter begin, and some guidance might have been furnished regarding the determinations which are required in sanitary and industrial analyses respectively. The occurrence of lead, copper, and zinc is not discussed. The analytical methods detailed in the next chapter are concerned with sewage and its treatment, and those in the one following with waters into which trade wastes and effluents have been discharged. In the references to chlorination there is no mention of its modern development, chloramination.

The analytical methods are set out in commendably clear language, and may be amplified by references which are easily found in the three chapters which succeed them. These chapters give particulars of the reagents used, some general chemistry, an account of the chemistry of water clarification and that of softening by the lime-soda process, and an outline of the chemistry of the analytical methods. The chemical section concludes with chapters discussing sampling and other matters, and tables of useful data. The inclusion of the specimen forms, which are said to follow the adjuration that all records should be in a bound book, has been overlooked. The order of the material in some of the later chapters could be re-arranged with advantage.

Much of the bacteriological section is devoted to basic technique. In the directions for sampling it is gratifying to note the insistence on the frequently neglected precaution to dechlorinate chlorinated waters immediately after collection. The scheme for bacteriological examination is described very clearly; it is confined to determining the presence of absence of the coli-aerogenes group as a whole and does not include differentiation as to type.

The book contains much useful information for all who have to deal technically with water and sewage, but for the practising analyst in particular its utility is subject to some limitation owing to the absence of any adequate discussion of the interpretation of results. ROBERT C. FREDERICK

DIE CHROMATOGRAPHISCHE ADSORPTIONSMETHODE. By L. ZECHMEISTER and L. v. CHOLNOKY. Pp. xi + 231. Vienna: Julius Springer. 1937. Price RM.14.40.

Those chemists who still think that chromatographic analysis is a vicious method, more likely to destroy than to isolate the compound sought, should read this book. True, there are instances of compounds being destroyed on a Tswett column and of decomposition products being isolated in their place, and examples are cited by the author. The rest of the book provides a powerful justification of the method, that can hardly fail to convince the most stubborn sceptic of its validity.

Devised thirty years ago by Tswett, a Russian botanist, the technique remained almost unnoticed and unused for twenty-five years, but within the last five years there has been carried out a great variety of work in which chromatography has been of paramount importance. This book gives the first comprehensive survey of the method that has so far been published. According to the authors, chromatography can be used as a test for homogeneity and for establishing the identity of an unknown with a known substance, for the concentration of a natural product occurring only in minute amounts, for the separation of the components of a mixture, for the purification of an impure substance and for the characterising and control of technical preparations.

The "general" part of the book consists of two chapters. The first, dealing with general principles, includes a discussion of what little is known of the theory of chromatography and a very illuminating account of the relation between structure and adsorption affinity. In the second chapter full details of the method are given, with descriptions of the various adsorbents and solvents, the types of apparatus and the different techniques adopted by various workers.

The "special" part, occupying almost two-thirds of the book, is a very clear and interesting survey of the applications of chromatographic analysis, and many classical experiments are described in full. These range from the large-scale preparation of chlorophyll, in which several kilograms of adsorbent were used, to the detection of erythropterin and xanthopterin in the wings of the Brimstone butterfly, using a tiny column only 1 mm. in diameter! The great variety of substances that have been successfully isolated by the method will be gathered from the following selection: chlorophyll and the carotenoids, synthetic dyestuffs, acetyl cellulose, carcinogenic compounds, alkaloids, enzymes, and most of the vitamins. It is unfortunate that the announcement of the use of the method for separating the rare earths came just too late to be included.

Several tables are given, showing the compounds that have been isolated from a variety of vegetable and animal sources, and there is a useful list of formulae of most of the carotenoids and some excellent photographs of chromatograms, as well as a long bibliography, complete to the end of 1936, and a good index.

Criticism may seem ungracious, but surely a more serviceable binding than the present paper cover could have been provided. It is a pity, too, that vitamin B_2 and lactoflavin are given as synonymous terms, and that ergosterol is described as the provitamin D associated with cholesterol.

It must be pointed out that chromatographic analysis is not a research weapon only, for instances are given of its employment in general analytical work. The detection of artificial colouring matter in wine and the detection of sophistication in pharmaceutical preparations illustrate this, and one might add that the determination of the biologically important β-carotene in presence of inactive carotenoids is difficult, or impossible, by other methods. It is certain that many other applications of this simple and elegant method are awaiting discovery. No better guide than this book can be imagined. It is to be hoped that an English translation will soon make its appearance, for such a useful book should be readily accessible to all chemists.

F. A. ROBINSON

MAY, 1937 Vol. 62, No. 734

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 7th, 1937, the President, Dr. G. Roche Lynch, in the chair.

Certificates were read in favour of Robert Alwyn Bottomley, B.Sc., A.A.C.I., Paul Haas, D.Sc., Ph.D., David Alexander Lambie, B.Sc., A.I.C., Harry Morris Rainey and George Robertson Howat, B.Sc., Ph.D.

The following were elected members of the Society:—Joseph John Blackie, Ph.D., F.I.C., Ph.C., Harold William Christian, B.Sc., A.I.C., Walter Edward Green, B.Sc., Norman Heyworth Law, M.Sc., A.I.C., Leonard Thornton Lowe, B.Sc., A.I.C., Peter John Markham, B.Sc., A.I.C., Hubert Alfred Parkes, B.Sc., F.I.C. and Robert Charles Tranent.

The following papers were read and discussed:—"Quantitative Microscopical Analysis of Feeding Stuffs: I. Determination of Rye, Wheat and Barley Starches in Mixtures; Ground Oats Mixtures," by J. G. A. Griffiths, B.A., Ph.D., A.I.C.; "The Hartridge Reversion Spectroscope: Improvements in Design, Assembly and Technique," by R. C. Frederick, F.I.C.; "The Properties of Calciferol," by F. W. Anderson, B.Sc., A.I.C., A. L. Bacharach, M.A., F.I.C., and E. Lester Smith, D.Sc., F.I.C.

NORTH OF ENGLAND SECTION

A meeting of the above Section was held at Sheffield on April 10th. In the absence of the Chairman (through illness) and the Vice-Chairman, Dr. Dunn presided over an attendance of twenty-four.

The following papers were read and discussed:—"The Acidity of Paper," by D. Burton, M.B.E., D.Sc., F.I.C., and "The Spoilage of Flour," by D. W. Kent-Jones, Ph.D., B.Sc., F.I.C.

The Alkaloids of Ergot

BY GEORGE BARGER, HON. D.SC., HON. M.D., LL.D., F.R.S.

(Address given at the Annual General Meeting, March 5, 1937)

LIKE many other drugs, ergot owes its therapeutic and toxic properties to alkaloids. It yields four pairs of interconvertible isomerides, each pair consisting of a laevorotatory alkaloid having a powerful pharmacological action, and a strongly dextrorotatory one with but little pharmacological activity. The following table gives for each alkaloid the year of its discovery, and the value of $[\alpha]_{546\cdot1}$ (after Smith and Timmis):

Pharmacologically potent			Almost inert		
Ergotoxine (1906)	−226°	⇌	Ergotinine (1875)	+466°	$C_{35}H_{39}O_5N_5$
			⇅		
			ψ-Ergotinine (1931)	+513°	
Ergotamine (1920)	−181°	⇌	Ergotaminine (1920)	+450°	$C_{33}H_{35}O_5N_5$
Ergosine (1936)	−193°	⇌	Ergosinine (1936)	+522°	$C_{30}H_{37}O_5N_5$
Ergometrine (1935)	−16°	⇌	Ergometrinine (1936)	+596°	$C_{19}H_{23}O_2N_3$

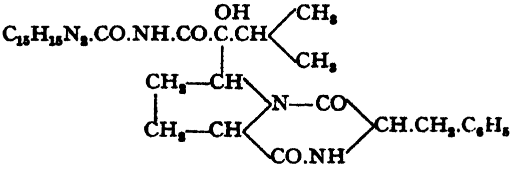
Associated with the first pair is an additional alkaloid of high dextrorotation (Smith and Timmis[65]), so that there is in reality a triplet; perhaps a third isomeride may later be added to the other pairs also.

Ergoclavine ($[\alpha]_D^{22}+124°$) is, according to Küssner,[49] a molecular compound of an alkaloid, $[\alpha]_D-149°$, resembling ergotoxine, and one with $[\alpha]_D+410°$, resembling ergotinine, for which the name ergoclavinine is suggested; this homogeneous well-crystallised substance is doubtless an equimolecular compound of ergosine, $[\alpha]_D^{20}-161°$, and ergosinine $[\alpha]_D^{20}+420°$; this view is supported by the products of its hydrolysis. Sensibamine is, according to Stoll,[78,79] a similar but much less stable molecular compound of ergotamine and ergotaminine; on mere solution in alcohol or acetone, the latter alkaloid crystallises out. The mixture can also be separated by chromatographic adsorption. All the above-mentioned alkaloids have been crystallised. Simple bases, insoluble in ether, such as ergothioneine, uracil, guanosine and amines derived from amino acids, have been excluded from this review.

The four pairs of isomeric alkaloids are particularly well characterised, and, in spite of their complexity, the molecular formulae have in all cases been established with certainty and confirmed by hydrolysis. This is due largely to the admirable work, during the last few years, of Jacobs and Craig[30-40] in the United States, and of Smith and Timmis[64-72] in this country. As an example, ergotinine yields with aqueous alkali one equivalent of ammonia (Soltys[74]), isobutyryl formic acid $(CH_3)_2CH.CO.COOH$ and one equivalent of lysergic acid $C_{16}H_{16}O_2N_2$ (Jacobs and Craig[31,32]), or with alcoholic sodium hydroxide these fragments may remain combined as the amide of lysergic acid, or ergine, $C_{16}H_{17}ON_3$ (Smith and Timmis[66,68]). Acid hydrolysis destroys lysergic acid (which is an indole derivative) and yields *l*-phenylalanine and *d*-proline. It is thus possible to deduce the following equation:

$$C_{35}H_{39}O_5N_5 + 4H_2O = C_{16}H_{16}O_2N_2 + NH_3 + C_5H_8O_3 + C_9H_{11}O_2N + C_5H_9O_2N.$$

The exact arrangement of the various fission products is not known. The lysergic acid is certainly joined to the ammonia (because of the formation of ergine); the isobutyryl formic acid is also joined by its carboxyl to an amino group, for, on pyrolysis, isobutyryl formamide sublimes (Barger and Ewins[6]). The nitrogen atom in the latter amide need not, however, be that giving rise to ammonia, but may be the nitrogen atom of phenylalanine; the two amino acids are also joined together, for their dipeptide has been isolated as a result of moderate hydrolysis. The following formulae for ergotinine have been suggested by Turner[86]:



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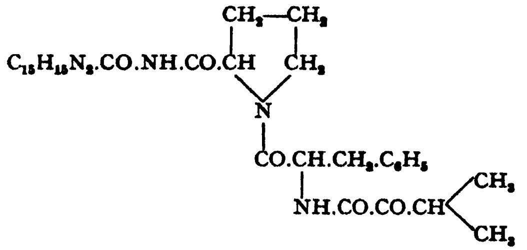


II

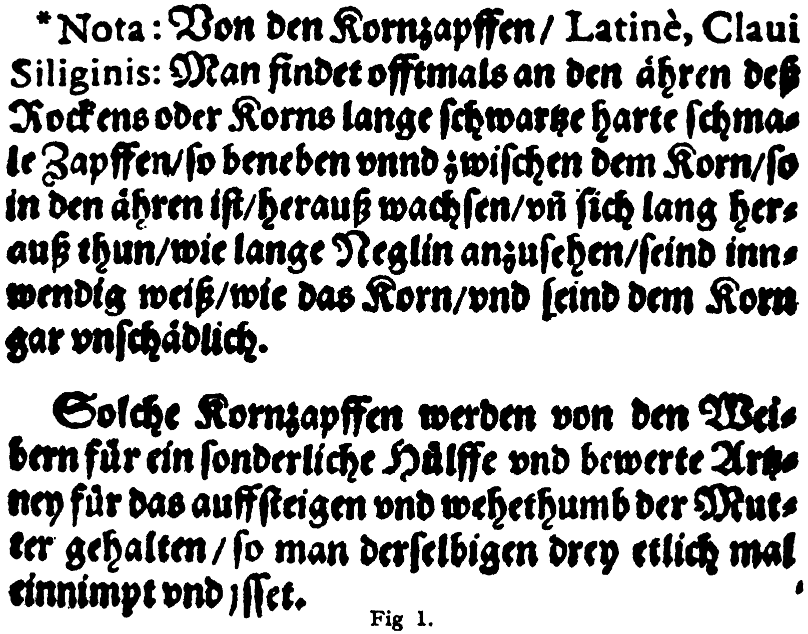
The only difference between ergotoxine-ergotinine and ergotamine-ergotaminine is that the latter pair give rise to pyruvic instead of isobutyrylformic (= dimethyl pyruvic) acid. Since the rest of the large molecule is the same, the great similarity in the pharmacological action of ergotoxine and ergotamine becomes intelligible. The third pair of alkaloids also yields pyruvic acid, but here the phenylalanine is replaced by leucine. (These same two products, but not *d*-proline, were obtained from ergoclavine by Jacobs and Craig[37,40].) Ergosine and ergoclavine have a pharmacological action closely resembling that of ergotamine and ergotoxine, but the presence of leucine, instead of phenylalanine, gives rise to some quantitative differences, as between ergosine on the one hand and ergotamine and ergotoxine on the other. The latter two, and probably all three, can produce gangrene; all three inhibit the action of adrenaline. In this respect they differ entirely from the active alkaloid of the last pair: ergometrine has no such specific pharmacological actions, and for this reason escaped the attention of pharmacologists. It was only discovered by exact clinical experiments, for its outstanding property is rapidly to bring on powerful contractions of the puerperal (human) uterus. This is the only specific biological test for the substance, and ergometrine is *par excellence* the long-sought therapeutic principle of ergot. The great biological difference from the other alkaloids (which indeed also cause contraction of the uterus, but more slowly) is due to a considerable difference in structure and to a much smaller molecular weight which favours rapidity of absorption; ergometrine gives, on hydrolysis, two products only, lysergic acid and a simple amine, α-hydroxy-β-aminopropane[26]:

$$C_{19}H_{23}O_2N_3 + KOH = C_{15}H_{15}N_2.COOK + NH_2.CH(CH_3).CH_2OH.$$

The fission products of the various ergot alkaloids are recorded in the following table:

	Ergotoxine Ergotinine	Ergotamine Ergotaminine	Ergosine Ergosinine	Ergometrine Ergometrinine
Lysergic acid	+	+	+	+
Ammonia	+	+	+	
Hydroxyisopropylamine	−	−	−	+
d-Proline	+	+	+	−
l-Phenylalanine ..	+	+	−	−
l-Leucine	−	−	+	−
Dimethylpyruvic acid	+	−	−	−
Pyruvic acid	−	+	+	−

It is of interest to note that the complicated alkaloids of ergot differ rather considerably from the alkaloids of the higher plants; the first three pairs are akin to polypeptides and contain, indeed, two amino acids apiece. In respect of its alkaloids, as in respect of many simpler constituents, ergot presents points of unusual biochemical interest. The phenylalanine of ergotoxine and ergotamine, and the leucine of ergosine are optically identical with fission products of protein, but the *d*-proline in all three is the enantiomorph of the *l*-proline obtained by protein hydrolysis. Butyryl formic (=dimethyl pyruvic) and pyruvic acids are



*Nota: Von den Kornzapffen / Latinè, Claui Siliginis: Man findet offtmals an den áhren deß Rockens oder Korns lange ſchwartze harte ſchmale Zapffen/ſo beneben vnnd zwiſchen dem Korn/ſo in den áhren iſt/herauß wachſen/vñ ſich lang herauß thun/wie lange Neglin anzuſehen/ſeind innwendig weiß/wie das Korn/vnd ſeind dem Korn gar vnſchádlich.

Solche Kornzapffen werden von den Weibern für ein ſonderliche Hülffe vnd bewerte Artzney für das auffſteigen vnd wehethumb der Mutter gehalten / ſo man derſelbigen drey etlich mal einnimpt vnd iſſet.

Fig 1.
First mention of ergot and of its therapeutic properties in Adam Lonicer's Kreuterbuch, Frankfurt on Main, 1582

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* *Translation.*

NOTE.—On Corn Spurs: Latin *Clavi siliginis* (*Nails of Corn*):—There are often found on the ears of rye or corn long black hard narrow spurs, being close to, and between the corn, that is to say, in the ears, growing out of them, and extending out so that they look like long nails; they are white inside like corn and are quite harmless to the corn.

Such corn spurs are regarded by women as a particularly useful and valuable remedy for swelling and pains of the womb; for this purpose they are taken about three times and eaten.

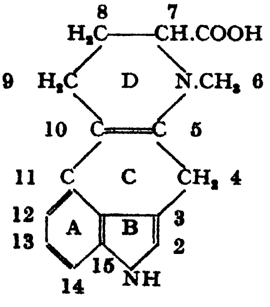
further closely related to the amino acids valine and alanine, respectively, and lysergic acid is doubtless derived from tryptophane, by the addition of a chain of five carbon atoms which may represent yet another amino acid residue. The hydroxyisopropylamine of ergometrine may be regarded as a reduction product of alanine ("alanol").

It is necessary now to consider the constitution of lysergic acid, the most characteristic fission product, and the only one common to all four pairs of alkaloids. Lysergic acid and its simple amide ergine have been obtained in two forms, corresponding to the two series of potent and of inert alkaloids. The following table illustrates this by the values of $[\alpha]_{546\cdot 1}$ in pyridine according to Smith and Timmis[71]:

Ergometrine	−16°	Ergometrinine	+596°
Iso-ergine	+25°	Ergine	+635°
Lysergic acid	+49°	Iso-lysergic acid	+365°

It will be seen that the ergine first obtained belongs to the ergotinine series, and the (first) lysergic acid, originally discovered by Jacobs and Craig, is analogous to ergotoxine. Ergometrine and ergometrinine can be partially converted into each other by boiling *N* alcoholic potassium hydroxide solution; some hydrolysis to lysergic acid always occurs, but is evidently slower than the conversion into the other alkaloid (Smith and Timmis[70]). The isomerism of these substances and of the other pairs of ergot alkaloids clearly depends on the lysergic acid portion, and seems to be determined by a shift of a double bond, the only one known to occur in this acid. Jacobs and Craig[89] reduced (laevorotatory) ergotoxine, ergotamine and ergometrine catalytically, and then obtained α-dihydrolysergic acid, $[\alpha]_D$ −106°, also obtained by reducing lysergic acid itself; on the other hand, the dextrorotatory ergotinine and ergotaminine are, after reduction, hydrolysed to γ-lysergic acid $[\alpha]_D$ +33°. (β-Lysergic acid is yet another substance, obtained in a different way.) Jacobs and Craig consider that in the dihydrolysergic acids a stereoisomerism has become fixed by the abolition of the double bond; the dihydro acids are not interconvertible; the methyl ester of lysergic acid shows mutarotation in hot methyl alcohol, the esters of the dihydro acids do not.

The constitution of lysergic acid has not yet been fully established, but a formula suggested by Jacobs and Craig[89] is doubtless so near the truth that it may serve to illustrate the main features of the structure.



Rings A and B, with carbon atoms 4 and 5 and the upper nitrogen, form a tryptamine residue which has been isolated as such from a number of other alkaloids (calycanthine, evodiamine, strychnine). The α-position of the pyrrole ring (2) is unsubstituted, which accounts for the Hopkins and Cole and other colour reactions of the ergot alkaloids. The much employed reaction with *p*-dimethylaminobenzaldehyde is, however, so intense and peculiar that it may well be conditioned by a feature which has so far not been encountered in alkaloidal chemistry, namely, the ring closure with hydrogenated C_{11} of the benzene ring; in all other indole alkaloids of known constitution this carbon atom is not shared by a second ring. There are two reduced rings, C and D, which on distillation with soda lime survive together as quinoline. Potash fusion of dihydrolysergic acid yields 1-methyl-5-amino naphthalene, in which rings A and C survive with carbon atom 9 (the methyl group) and the indole nitrogen atom. Oxidation of lysergic acid yields a tribasic acid, $C_{14}H_9O_8N$, in which carbon atoms 2, 12 and 15 become carboxylated and the original carboxyl at 7 becomes combined with the nitrogen at 6 to form a quinoline-betaine. The latter nitrogen bears the one *N*-methyl group of ergot alkaloids, and is the only basic one; the carboxyl group at 7 is present in an amide grouping in the alkaloids. The position of the double bond is placed tentatively between C_5 and C_{10}, and Jacobs and Craig imagine that in mutarotation it shifts to 9–10 and/or 4–5, but its position in the two lysergic acids and their relationship is still uncertain.

The rapid and remarkable advance in our knowledge of the ergot alkaloids during recent years has, as it were, rounded off the subject and has allowed of a brief presentation of the main results in tabular and diagrammatic form. It may, perhaps, be of interest to consider now also the difficulties which retarded progress in the past. The possibility of isomerism in the lysergic acids not only gives rise to opposite optical rotation, and to a great difference in pharmacological potency in the two series of alkaloids, but also brings about a difference in their power of crystallising. The inert alkaloids are sparingly soluble in organic solvents and crystallise readily without solvent of crystallisation. The potent alkaloids, on the other hand, have a remarkable power of forming additive "compounds" with the solvent, and with isomeric inert alkaloids (ergoclavine and sensibamine are such crystalline molecular "compounds"). It is therefore natural that the first alkaloid, ergotinine, crystallised by the French pharmacist Charles Tanret in 1875,[84] belongs to the almost inert series, and that he regarded a potent alkaloid present in the mother liquors of ergotinine as merely an amorphous and impure variety of the crystalline. This explains a prolonged controversy about the pharmacological action of ergotinine, which controversy becomes the more intelligible when we consider that ergotinine is readily transformed into the potent ergotoxine. The high molecular weight and residual valency of the latter alkaloid for a long time prevented its recognition as a separate substance, and during the three decades which followed Tanret's discovery pharmacologists (Kobert,[45] Jacobj[39]) attributed the gangrenous and other actions of ergot, not to an alkaloid, but to amorphous acidic and phenolic substances which, as we now know, owed their activity to adsorbed ergotoxine; the latter is a weak base having also acidic properties. Dale,[10] indeed, began his fundamental work on the pharmacology of ergot with such a substance (chrysotoxin) containing about 2 per cent. of adsorbed ergotoxine. The separation of the latter is complicated by the fact that the salts of ergotoxine are little soluble in water and are precipitated from their colloidal solutions by electrolytes, notably by excess of mineral acids. Strong acids should accordingly be avoided in the chemical assay of the alkaloids, which have often been weighed mixed with non-alkaloidal substances. Ergotoxine, the most abundant active alkaloid in ergot, was isolated as crystalline phosphate by Barger and Carr.[4,5] Its existence was recognised independently by Kraft,[46] who obtained from ergotinine the sparingly soluble sulphate of another alkaloid which he regarded as formed from ergotinine by hydration (hydroergotinine). The additional molecule of water seemed to be confirmed by analyses of crystalline ergotoxine salts (Barger and Carr[5]), but I now incline to the view of Stoll and others, that ergotoxine is not a hydrate of ergotinine, but isomeric with it. Much later ergotoxine was crystallised as free base by Smith and Timmis[64]; for this purpose it should be liberated from its salts by sodium bicarbonate or borate, not by sodium carbonate, and the only suitable solvents for crystallisation are benzene and carbon bisulphide. These are so tenaciously retained in the crystals that, even now, no concordant analyses of this alkaloid have been published.

Ergotamine (Stoll[77]) crystallises with a variety of solvents—particularly well from aqueous acetone with $2H_2O.2C_3H_6O$. Its salts are generally rather more soluble than those of ergotoxine. In alcoholic solution it shows mutarotation (Frèrejacque and Raymond-Hamet[17]), with partial conversion to ergotaminine (Stoll[77]). The latter alkaloid crystallises, without solvent, in characteristic triangular leaflets, and is probably the least soluble of all ergot alkaloids (1:6400 in alcohol at room temperature).

Ergosine and ergosinine were discovered by Smith and Timmis[69]; I am greatly indebted to these authors for further details from a paper since published[72]. Ergometrine differs from the more complex alkaloids in being moderately soluble in water, and only very sparingly soluble in chloroform. This, and its lack of characteristic pharmacological properties, account for its having been overlooked for so long. Its existence in aqueous extracts of ergot was first recognised through the clincial experiments of Moir,[55] and it was then isolated by (Dudley and) Moir.[14] As the result of Moir's first publication a water-soluble principle was sought for and found by several other workers; the crystalline substance was described in successive months (March–June, 1935) as ergometrine by Dudley and Moir, as ergotocine by Kharasch and Legault,[43] as ergobasine by Stoll and Burckhardt,[81] and as ergostetrine by Thompson.[85] After an exchange of specimens these various substances have been recognised, by those concerned, to be identical (Kharasch, King, Stoll and Thompson[44]). There seems little doubt that the priority, both biological (1932) and chemical (1935), belongs to Dudley and Moir, and that the alkaloid should therefore be called ergometrine. It crystallises with a variety of solvents, some of which (benzene, methyl ethyl ketone) are given off completely in a high vacuum at 100° C., and, when thus freed from solvent, ergometrine melts at 162–3° C. It also crystallises in this condition from ethyl acetate at $-4°$ C., but at room temperature it forms different crystals with 0·5 mol. of ethyl acetate, which is so tenaciously held that this second variety melts with effervescence, but without darkening, at 130–132° C. This ethyl acetate compound is more stable to atmospheric oxygen than the crystals containing benzene or ethyl methyl ketone (Dudley[13]). By the action of acids or alkalis ergometrine is partially converted into the inert ergometrinine (Smith and Timmis[70]), which is much less soluble in water, and much more soluble in chloroform than ergometrine, into which it can be partially re-converted by acids and alkalis. It crystallises without solvent of crystallisation.

The remarkable difference in pharmacological properties, optical rotation and power of associating with solvents, which the two series of ergot alkaloids exhibit as a result of an isomeric change in the lysergic acid portion of the molcule, is a phenomenon of considerable interest, and excites curiosity as to what exactly is the nature of the isomerism. The residual valency which the active series evidently possesses is, perhaps, also responsible for the pharmacological action by anchoring the alkaloids to the cells on which they act. Further chemical knowledge of the constitution of lysergic acid may perhaps ultimately lead to a deeper insight into the reason *why* drugs act.

Ergoclavine (Küssner[48]) is probably an equimolecular mixture of ergosine and ergosinine, and sensibamine (Chinoin A.G. and Wolf[9]) a similar mixture of ergotamine and ergotaminine. An alkaloid, $C_{19}H_{19}O_4N$, is described by Holden and Driver,[27] who state that it is not an indole derivative.

The first, third and fourth pairs of alkaloids seem to occur in all specimens of ergot of rye, but it should be emphasised that the second pair is absent from most specimens of the drug, and occurs only in ergot of rye from a particular source. Their discoverer, Stoll, has declared this source to be "Central Europe," and we may take it to be Hungary, for sensibamine (according to Stoll a mixture of ergotamine and ergotaminine) was discovered there, and Hungarian ergot was the *only one reported on by Küssner[48] which yielded these alkaloids. Smith and* Timmis examined a large number of commercial specimens of ergot of rye from many countries, and always isolated the first pair of alkaloids and never the *second. They obtained,[64] however, ergotamine and ergotaminine, and these* only, from a non-official ergot, *Claviceps purpurea* growing on *Festuca elatior* in New Zealand. They employed the simple ether extraction method of Kraft, and accordingly consider that the isolation of ergotamine and ergotaminine does not depend on the special method of extraction devised by Stoll, but on the nature of the ergot. It would be interesting to know more about the biological peculiarities of the Hungarian ergot yielding these alkaloids.

Since the two alkaloids in the various pairs are readily transformed into each other, it is a matter of doubt to what extent each occurs as such, or arises during the process of separation. Stoll considers that ergotaminine does not occur in ergot as such, and is a secondary product formed during extraction. Ergometrinine has only been obtained with difficulty from ergometrine mother liquors and may be formed in similar fashion. The relative proportion of the other alkaloids is by no means constant. Küssner,[48] before the discovery of ergometrine, gives the following examples, as percentages of total crude alkaloid actually crystallised:

	Ergotinine	Ergotoxine phosphate	Ergoclavine	Total
Spanish ..	37·6	11·5	19·3	68·4
Do. ..	31·2	15·5	18·5	65·2
Do. ..	29·0	18·7	15·8	63·2
Russian ..	45·5	10·0	19·9	75·4

On the assumption that ergoclavine is an equimolecular mixture of ergosine and ergosinine, the ratio of inactive to active alkaloid varies from 1·4 to 2·2, but it may well be lower. The amount of ergometrine in Spanish ergot is considered by Smith and Timmis (private communication) to be 10 to 15 per cent. of the total, but assays by Hampshire and Page[24] indicate a somewhat higher proportion (about 20 per cent.).

The pharmacologically potent alkaloids (ergotoxine, ergotamine, ergoclavine, ergosine) all antagonise the action of adrenaline in much the same way, and, since chemical and physical assay methods cannot distinguish between these and their almost inert isomerides, the only reliable way of standardising ergot preparations is by biological methods, best by that of Broom and Clark[7] on the isolated rabbit's uterus. The chemical determination of total alkaloid, indeed, gives a useful rough indication of the value of a particular ergot, for the proportion of inactive to active alkaloid does not vary excessively (see above).

The discovery of ergometrine, the therapeutically important principle, has further complicated the question, for there is no pharmacological method for its assay. Again, on the assumption that the proportion of ergometrine to the other alkaloids does not vary greatly (it seems to be something like 1:6), chemical assays of total alkaloid give some indication, but an accurate chemical method of assaying ergometrine separately is very desirable and seems quite possible (see below).

CHEMICAL AND PHYSICAL METHODS OF ASSAY.—These may be divided into:

(1) Chemical *methods in which the alkaloids of the first three groups* are either weighed or titrated.
(2) A colorimetric method depending on the lysergic acid grouping, which, therefore, *seems to give identical colorations for equimolecular amounts* of all four groups (including ergometrine).
(3) Spectrophotometric methods which do the same as (2).
(4) A method assaying separately the water-soluble alkaloid ergometrine.

(1) *Chemical Methods.*—The oldest is that of the Swiss pharmacist, Keller,[41,42] and the prototype of most present-day processes of alkaloidal assay, depending on the extraction from ethereal solution by acid, and, after making alkaline, shaking out again with ether, evaporating, and weighing the residue. This process, as applied to ergot, has been modified by Fromme,[20] but even after this modification it is open to objection. Meulenhoff[53,54] and Harmsma[25,26] have pointed out that when the first ethereal solution is shaken with hydrochloric acid, a crystalline precipitate of an alkaloidal hydrochloride is formed which Fromme filters off and discards; hence, tartaric acid should be used instead of mineral acids. (Ergotoxine salts are precipitated by electrolytes.) A much more serious error in the opposite direction has been pointed out by Oettel[57] and by van Pinxteren[58]: the final ethereal residue may contain much inert matter and the results may be much too high. This error affected the older assays, which sometimes indicated an alkaloidal content as high as 0·4 per cent., never found in recent years. It is difficult to separate the alkaloids from a yellow colouring matter (see above, Jacobj[29] and Kraft[46]). If the alkaloids are precipitated by sodium carbonate and filtered off,

the results are lower and near the truth; this procedure is adopted by the German Pharmacopoeia, in order to eliminate water-soluble amines (Gadamer and Neuhoff[21]). Whilst the amines do not appreciably pass into ether, the filtration favours the separation of alkaloids from the yellow colouring matter, which is soluble both in ether and in sodium carbonate solution. The use of ammonia has been suggested for the liberation of the alkaloids, but, since ergotoxine begins to dissolve at *p*H 8, this should be avoided; a buffer mixture (0·2 mol. of disodium hydrogen phosphate + 0·1 mol. of citric acid) is recommended by van Pinxteren. The latter author prefers weighing the alkaloids to the titration recommended by the German Pharmacopoeia, on the ground that the voluminous precipitate adsorbs sodium carbonate, which, owing to its equivalent being one quarter of that of the alkaloids, causes, when included in the titration, an error four times as great as that due to weighing it. Schlemmer, Wirth and Peters[62] recommend a micro-Kjeldahl estimation of the crude alkaloidal residue; here all five nitrogen atoms of the alkaloids are converted into ammonia and give five times the titration value of the alkaloids themselves, which are monacidic bases; moreover, the non-nitrogenous colouring matters do not affect the result after destruction by the Kjeldahl method. With the above-mentioned modifications the Keller-Fromme method, like that of the German Pharmacopoeia, is satisfactory, in the opinion of Van Pinxteren and of Schlemmer, Wirth and Peters; compare also Leinziger and Kelemen,[50] Prybill and Maurer,[60] as well as Gatty–Kostyal and Derlatka.[22] The procedure of the German Pharmacopoeia has been chiefly criticised by Oettel,[57] who has adapted for quantitative use a somewhat peculiar method of isolating the alkaloids (Forst[15]). With 50 per cent. aqueous alcohol or acetone the alkaloids are extracted from ergot (which is not de-fatted); as much as 500 grams is used. The evaporation of the alcohol or acetone, even at a low temperature, leads, according to van Pinxteren, to decomposition of alkaloids and to low results. Schlemmer, Wirth and Peters to some extent confirm this, but do not consider the error to be serious. In any case the Oettel process is complicated.

In the method of Goris and Liot[23] the alkaloids are precipitated with silicotungstic acid; the precipitate is ashed, and the weight of ash, multiplied by 0·74, gives the weight of alkaloid. According to van Pinxteren, this method has not received the attention which it deserves. In dilute solution the reagent causes only a colloidal turbidity (Harmsma), but, according to van Pinxteren, the suspension coagulates in an ice-chest, and can then be collected in a Gooch crucible, washed and ignited.

(2) Of late a *colorimetric method* has come into vogue and has been adopted by the British Pharmacopoeia. The original colour reaction of Tanret, greatly improved by Keller,[42] was made still more sensitive and specific by the use of *p*-dimethylamino-benzaldehyde (van Urk[87]). It thus becomes a true indole reaction, and can be used quantitatively (M. I. Smith[68]). The blue colour is due to the indole complex in lysergic acid, and the intensity of the colour is the same for equimolecular amounts of all the ergot alkaloids. In the original method, the blue colour is only developed fully on exposure to light or heat; hence Allport and Cocking[1] have suggested the addition of a trace of ferric chloride (first used in a different way by Keller), which at once gives the maximum colour. This modification is preferred, *e.g.* by Upsher Smith[73] and others. Freudweiler[18,19]

uses vanillin instead of *p*-dimethylamino-benzaldehyde; the red colour produced by the former aldehyde is said to be more intense than the blue due to the latter, and exposure to light is unnecessary for its development. For other papers on the colorimetry of ergot alkaloids see Lozinski, Holden and Diver,[51] Swoap, Cartland and Hart,[83] Stevens,[76] and Swanson, Powell, Stevens and Stuart[82]; these authors are all concerned with a comparison between the colorimetric and a biological method.

(3) *The ultra-violet absorption spectrum* of ergotinine was first determined by Brustier,[8] and used for the assay of the alkaloids by Harmsma,[25,26] van Itallie,[28] Wokes and Crocker,[88] Allport and Crews.[2] There is a maximum at 316–318$m\mu$ and a minimum at 272$m\mu$; practically the same curve has been found for all the alkaloids (for ergometrine by Allport and Crews; ergosinine has not been investigated). The advantage of the spectroscopic method is its delicacy (even 1 part in 500,000 can be estimated); the solutions employed need be only moderately pure.

A comparison of the various methods so far referred to has been made by van Pinxteren and by Schlemmer, Wirth and Peters.

(4) *The Separate Assay of Ergometrine.*—This has so far only been attempted by Hampshire and Page,[24] and apparently with some degree of success. The three methods of assay above referred to do not distinguish between ergometrine and the more complex alkaloids. Hence the rather pronounced differences in solubility between the former and the latter must be utilised. Hampshire and Page found that certain solvents (carbon tetrachloride and amyl ether) extract ergotoxine, ergotamine, etc., from pure aqueous solution, but not ergometrine; when applied to the impure mixture of alkaloids directly extracted from ergot, the separation was, however, incomplete. On the other hand, it was found possible to remove ergometrine, and this alkaloid only, from a crude mixture of total ergot alkaloids in ether, by repeated shaking with water, until the aqueous layer no longer gave the colour reaction with dimethylamino-benzaldehyde. The combined aqueous extracts and the alkaloids remaining in the ether are then separately estimated colorimetrically against ergotoxine as standard, and the amount of ergometrine is obtained by multiplying by the factor 0·538 (ratio of molecular weights). As an example, 10 g. of ergot yielded 0·0128 g. total alkaloids, of which 0·0019 g. was water-soluble. Added ergometrine was recovered satisfactorily. The percentage of ergometrine in the total alkaloidal content was found for samples of Spanish ergot to be 24, 16, 20, 20 and 19 per cent., for Russian 13 and 21 per cent.

TOXICOLOGY.—Although in larger doses ergometrine is poisonous, at least to animals, the characteristic symptoms of ergot poisoning must be mainly attributed to the more complicated alkaloids ergotoxine, ergotamine and ergosine, which by constriction of the blood vessels impede the circulation and thus cause gangrene. This condition has been produced experimentally in the cock's comb by repeated intramuscular injections of pure ergotoxine and ergotamine. This production of gangrene by pure alkaloids has been attempted only in a few other species, and mostly with little success. The alkaloids also have certain effects on the central nervous system which lend further support to the view that they were the active agents in the epidemics of human ergotism which raged in the Middle Ages, and have

*Von dem kalten Brandt.

O Anthoni heiliger Man/
  Warumb nimbſt dich der Arzney an?
So Gott dem Herrn gebürt die Ehr/
  Vnd keinem Menſchen ſonſt nit mehr.

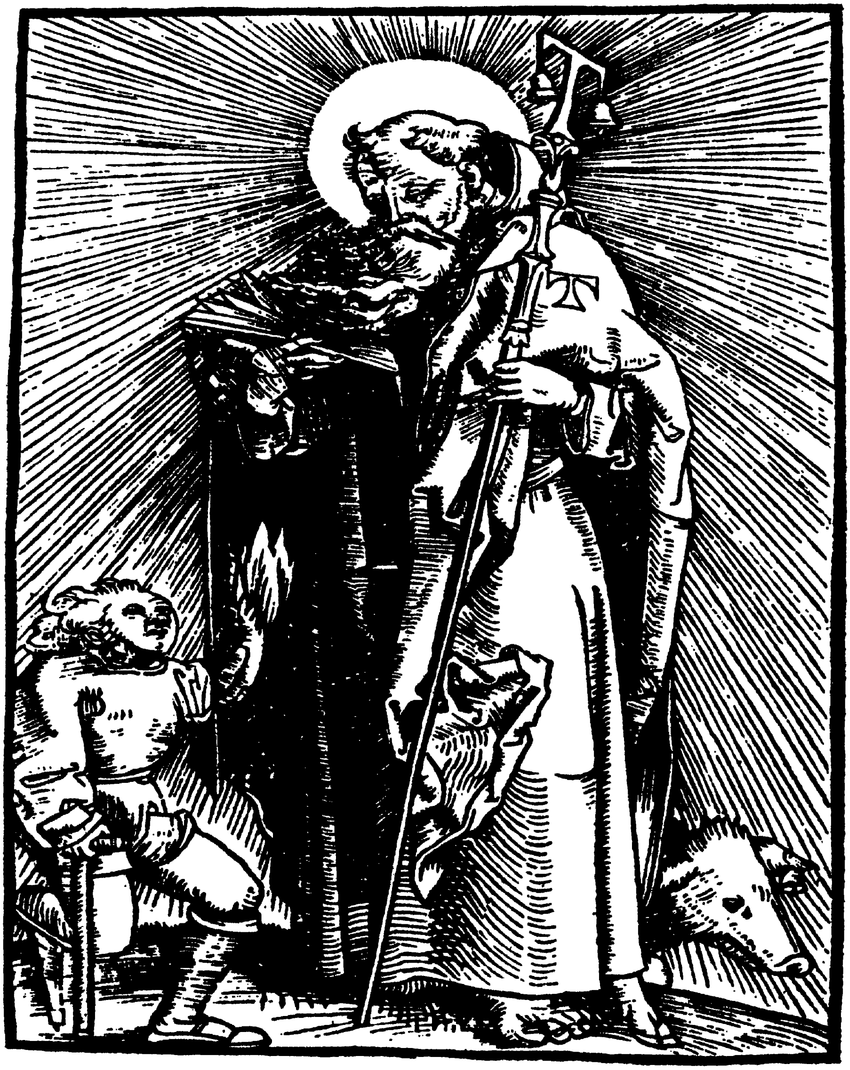


Fig. 2

Woodcut of St. Anthony with a victim of gangrenous ergotism, who has lost his right foot; the left hand burns with symbolical flames of St. Anthony's fire. From Gerrsdorff's book on military surgery, 1535.

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* *Translation*. ON "THE COLD FIRE" (GANGRENE)

O Anthony, thou holy man,
  Why dost thou claim the power to heal?
To God, the Lord, the honour's due—
  No longer now to any man.

occurred in a much milder form and on a much smaller scale even in recent years. Our knowledge concerning the toxic substances responsible for ergotism is, from the very nature of the disease, insecurely founded, and we are reduced to hypotheses and speculation.

There were two types of the disease which in their initial stages had a number of milder symptoms in common. The gangrenous type was characterised by violent burning pains in the part affected (more often a foot than a hand); hence the terms "fire of St. Anthony" and "holy fire," applied to the disease. After a time the pain was apt to stop, the diseased part became numbed and cold, and often black ("like charcoal," as the chronicles have it), and finally the mummified limb was generally detached at a joint, without pain or loss of blood. The extent of the gangrene varied from the mere shedding of nails and the loss of fingers or toes to that of several entire limbs. Apart from this loss, there were no other serious symptoms, and even in moderately severe cases the patient made a good recovery when placed on a wholesome diet.

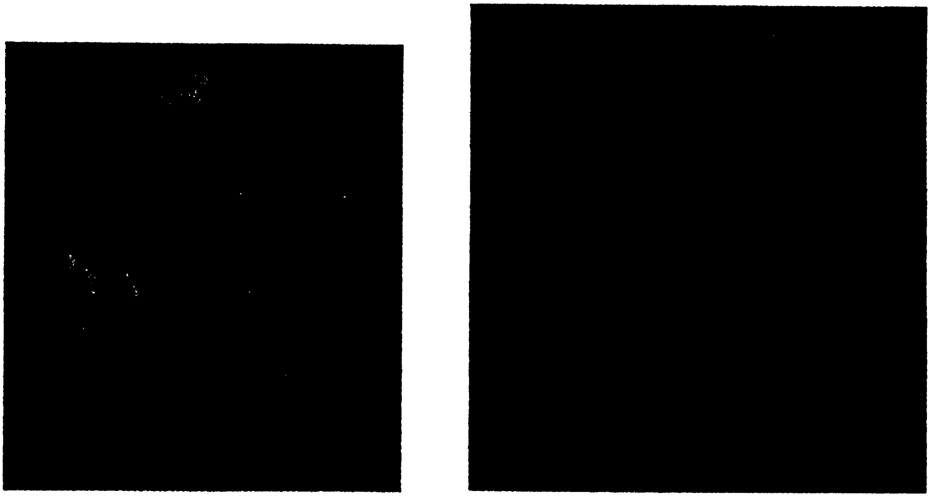

Fig. 3 Fig. 4

Frescoes in the Chapel of St. Anthony

Mural paintings from the chapel of St. Anthony, at Waltalingen, near Zürich (second half of fifteenth century). Fig. 3 refers to gangrenous ergotism (*cf.* Fig. 2). Fig. 4 represents an appeal to the Saint by sufferers from convulsive ergotism (*cf.* especially the hands with Figs. 6 and 7).

Convulsive ergotism was, on the other hand, not a vascular but a nervous disease, characterised by twitching and epileptiform convulsions, in the severest cases by delirium, blindness, deafness, paralysis and insanity. After one of the last epidemics (in Germany, 1879) a degeneration of the spinal cord was demonstrated by modern histological methods.

It is a remarkable fact that, although sometimes (*e.g.* in Russia) mixed epidemics occurred, gangrenous ergotism was confined chiefly to France, and the convulsive variety to Germany. An explanation may be sought tentatively in a difference in the diet of the poorest peasants of the districts affected. According to this hypothesis, gangrene is the primary effect of a prolonged administration of massive doses of the ergot alkaloids, which impede the circulation; the arterioles, as modern pharmacology has shown, become constricted. In convulsive ergotism a second factor would intervene and produce nervous symptoms with doses of ergot, not in themselves capable of causing gangrene. This second factor is most probably a deficiency of the fat-soluble vitamin *A* in the diet. E. Mellanby[52] has shown that ergot, and to a lesser extent wheat germ, produces lesions in the spinal cord of dogs, symptoms somewhat analogous to nervous ergotism in man. Probably the active agent of the ergot in this case is not an alkaloid, but a simpler substance.

If the above hypothesis as to the cause of convulsive ergotism is correct, it has to be shown that the diet of the poor French peasant was richer in vitamin *A* than that of the German. The literature of the eighteenth century on epidemics in these two countries supplies proof that such was the case. Even in the Sologne, formerly a damp and arid district of France (south of Orleans) where gangrenous ergotism was endemic, there were enough pasture, cows, milk, and butter. In the North German plain (*e.g.* in Hanover) contemporary records show that dairy produce was lacking in the diet of the labourers, and certain details in the description of German epidemics have almost the evidential value of a control experiment in showing that a shortage of vitamin *A* was a contributory cause of the disease.

For details concerning this point, and for a full historical account of ergotism, based as far as possible on contemporary sources, I would refer to my monograph on "Ergot and Ergotism"[3] from which the figures are reproduced by kind permission of the publishers. Certain problems still remain unsolved, and it is not even possible to advance hypotheses concerning them. Thus, whilst it is certain that rye was largely grown in England in the Middle Ages, ergot was so rare that there is no true English name for the fungus. (In the above monograph I have quoted close on 50 German names and some 17 French names.) Another question is why there are unmistakable references to gangrenous ergotism (in French chronicles) from the ninth and tenth century onwards, and yet there is no clear indication or description of convulsive ergotism in Germany before the end of the sixteenth century.

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Fig. 5

Gangrene of the Toes, due to Ergot.
Hungary, 1908

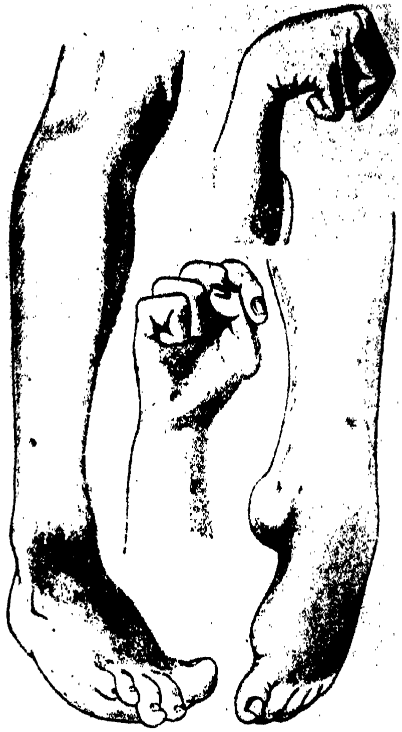

Fig. 6

Contractures of Hands and Feet.
From a dissertation by Heusinger, describ
the epidemic near Marburg, 1856

Fig. 7

Fatal Case of Convulsive Ergotism. Hungary, 1909

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The Average Vitamin *A* and Vitamin *D* Potency of Butter

BY (THE LATE) R. S. MORGAN, B.Sc., A.R.C.S., AND H. PRITCHARD, M.Sc.

WHEN we published in this journal (1935),[11] the results of our work on the vitamin potency and associated characteristics of average cod-liver oil, we were preparing for publication, on similar lines, the figures obtained during several years' work on the vitamin potency of butter. Mr. R. S. Morgan met with an untimely death before the work was quite completed, but it has now been collected and is published here, with additional data, as a posthumous paper.

The actual vitamin potency of butter is a most important subject, and it is surprising that since the establishment of the units of vitamins *A* and *D* on an international basis in 1931 few biological assays of butter in terms of these units have been published. On the other hand, there has been a good deal of work done with spectrophotometric and other non-biological methods for determining vitamin *A* and carotene, and this has led to the conclusion that during the summer, when the cows are at pasture, the vitamin *A* content of the butter increases to a maximum and then declines to a minimum in March or April. Bechtel and Hoppert[1] and others have shown that the vitamin *D* content also varies in much the same way, being at its maximum during the summer and falling to a minimum during the winter. The work now reported contains the results of biological assays of butter from several sources, collected over a period of years and tested against the international standard preparations for vitamins *A* and *D*. An attempt has been made to establish some relationship between the season and the average vitamin potency of butter as sold.

TECHNIQUE OF THE BIOLOGICAL ASSAYS.—The methods employed for determining biologically both vitamin *A* and vitamin *D* in butter were the same as those used in the work previously published by us on cod-liver oil.[11] These methods were worked out by R. S. Morgan, and descriptions of them have been published in full elsewhere.[9,10] The butters were mostly fed as such to the animals, but when the vitamin *D* potency was extremely low the determinations were made on the unsaponifiable matter only.

The standards used in the vitamin *A* assays were those issued by the League of Nations Permanent Commission on Biological Standardisation, and distributed by the Medical Research Council. In the earlier part of the period the mixed carotene issued in 1931 was used, but this was replaced later by the solution of pure β-carotene issued in 1934. For a short period subsidiary vitamin *A* standards were used. These had been accurately calibrated against both the 1931 and the 1934 carotenes.

It is impossible here to give details of every assay, or even the figures from which they were calculated, but, in order to illustrate the amount of experimental work involved and the manner in which the results were obtained, the figures for a typical butter have been given below, and the method of working out the assay. The butter chosen is one produced in September, 1935, on a Dutch farm, and is recorded in Table VI.

VITAMIN *A*.—The rats used in the assay were weaned on to a vitamin *A*-free diet, and were used for the test when the rate of growth began to slacken. Pairs were selected from the bucks of each litter; one of each pair received the standard and the other the butter. The doses of butter were chosen in the expectation of an assay of 25 units per gram. In the following table the results obtained during the three weeks' experimental period have been set out.

TABLE I

VITAMIN *A* ASSAY OF DUTCH BUTTER PRODUCED IN SEPTEMBER

	Standard			Butter			
Litter	Daily dose in international units	A Growth in grams in 3 weeks	A^2 Grams in 3 weeks	Daily dose in milligrams	B Growth in grams in 3 weeks	B^2 Grams in 3 weeks	A^2—B^2
1848	¾	43	1849	30	35	1225	624
1850	¾	35·4	1274	30	41	1681	—407
	1	40·3	1624	40	39·7	1576	48
	2	54·7	2992	80	56·4	3181	—189
1852	1	34·7	1421	40	43·7	1910	—489
	2	46·6	2172	80	42·3	1789	383
1855	1	34	1156	40	33	1089	67
1859	1	29·7	882	40	43·7	1910	—1028
1861	¾	27·7	767	30	46	2116	—1349
	1	36·3	1318	40	44·3	1962	—644
	2	41	1681	80	53·3	2841	—1160
1862	½	35·6	1267	20	34·6	1197	70
	1	52·3	2735	40	57	3249	—514
						Summation	—4588

Average pair difference for 13 pairs of rats = —353

The negative controls were rats from each litter receiving no dose and showed no growth.

It has been found from a large number of assays for vitamin *A* that the best relationship between increase of weight and the amount of vitamin administered is given by the expression

$$w^2 = n \log d + m$$

where w is the increase in weight, d the dose of vitamin *A*, and n and m two constants.

It follows that (for litter-mates)

$$w_1^2 - w_2^2 = n \log \frac{d_1}{d_2}$$

Experiment has also given to n an average value of 4082.

Consequently, from the figures in Table I, we get

$$353 = 4082 \log \frac{\text{dose of butter}}{\text{dose of Standard}}$$

and the dose-ratio is thus found to be 1·22, indicating that the true potency of the butter is greater than the expected value of 25 units per gram in the ratio 1·22 : 1, and is, therefore, 30·5 units per gram.

VITAMIN *D*.—Doses were chosen on the expectation of an assay of 0·5 unit per gram. The prepared rats were selected in pairs, in the same way as for the vitamin *A* assay, one receiving the International Standard Preparation of vitamin *D* and the other the daily dose of butter. After ten days the rats were killed and their radii and ulnae sectioned and stained with silver nitrate. The area of the "line" of newly-calcified bone was measured in square millimetres on the eleven-times magnified drawing. The results obtained for this butter are shown in Table II.

TABLE II

VITAMIN *D* ASSAY OF DUTCH BUTTER PRODUCED IN SEPTEMBER

	Standard			Butter			
Litter	Daily dose in international units	A Healing in sq.mm.	$A^{0·7}$	Daily dose in g.	B Healing in sq.mm.	$B^{0·7}$	$A^{0·7}$—$B^{0·7}$
1845	½	134	30·8	1·0	112	27·3	3·5
1848	¼	86	22·6	0·5	124	29·2	—6·6
	½	156	34·3	1·0	158	34·6	—0·3
1849	¼	70	19·5	0·5	88	22·9	—3·4
	¼	126	29·5	0·5	108	26·6	2·9
	½	150	33·4	1·0	230	45	—11·6
1858	½	172	36·4	1·0	170	36·4	0·3
1859	¼	4	2·7	0·5	32	11·3	—8·6
	½	108	26·6	1·0	120	28·6	—2
						Summation	—25·8

Average difference for 9 pairs = —2·86

The 5 negative controls showed no healing.

When this technique was first elaborated by Morgan (1932) consideration of the healing at 4 different levels of dosage in 151 animals gave similarly the straight-line equation

$$y_1 - y_2 = k \log \frac{x_1}{x_2}$$

where $(y_1 - y_2)$ was the difference in healing between two litter-mates dosed in the ratio x_1/x_2.

The subsequent inclusion of several hundreds more animals in the statistical data revealed that closer conformation to a straight-line relation was given by

$$y_1^{0\cdot7} - y_2^{0\cdot7} = k \log \frac{x_1}{x_2}$$

which equation has been employed in the results here presented, using for k the experimentally found value of 55·2. Then from the figures in Table II, we get

$$2\cdot86 = 55\cdot2 \log \frac{\text{dose of butter}}{\text{dose of Standard}}.$$

This means that the true potency of the butter is greater than the expected value of 0·5 unit per g. in the ratio 1·127 : 1 and is, therefore, 0·56 unit per gram.

RESULTS.—The results of the biological assays have been classified into several groups, according to the source of the butter, and are shown in the following tables. The moisture-content has also been recorded wherever possible. Table III records the vitamin *A* assays of a number of dairy butters purchased in London.

TABLE III

VITAMIN *A* POTENCY OF DAIRY BUTTERS PURCHASED IN LONDON

Date of purchase		International units of vitamin *A* per gram of butter	Moisture-content of butter Per Cent.
September	1932	23·4	—
March	1933	25·0	—
May	,,	25·4	—
July	,,	21·0	—
August	,,	28·6	—
September	,,	22·9	—
October	,,	22·0	—
December	,,	28·4	13·6
June	1935	24·8	12·0
July	,,	27·8	15·0
August	,,	32·1	13·1
,,	,,	30·2	12·5
October	,,	23·6	13·6
November	,,	31·6	13·3
January	1936	35·6	14·0
,,	,,	30·9	13·6
February	,,	38·6	14·0
March	,,	34·0	12·8
April	,,	36·1	12·5
May	,,	35·4	8·0

Set out in the next table are the vitamin *A* and vitamin *D* assays of miscellaneous samples of butters to be found on the market in England.

TABLE IV

MISCELLANEOUS SAMPLES OF BUTTER

Description of butter				International units per gram of butter		Moisture-content of butter Per Cent.
				vitamin *A*	vitamin *D*	
New Zealand:	Purchased	Jan.	1932	—	0·30	—
	,,	June	,,	24·0	0·57	—
	,,	Aug.	1933	23·4	—	—
Danish:	,,	Jan.	1932	—	0·18	—
	,,	Aug.	,,	—	0·085	—
	,,	,,	1933	20·9	—	—
	,,	Dec.	1934	13·4	—	11·8
	,,	May	1935	10·0	—	11·3
English:	Produced	Oct.	1933	20·7	—	17·9
	,,	,,	,,	18·8	—	17·1
	Purchased	Aug.	1932	—	0·67	—
	Produced	June	,,	—	0·63	—
	,,	July	,,	—	0·46	—
Irish:	Purchased	Oct.	,,	—	0·50	—
Scottish:	,,	April	1936	10·2	Not more than 0·09	11·7
	,,	May	,,	20·9	0·29	14·5
	,,	,,	,,	12·4	0·21	16·0
Dutch:	Produced	,,	,,	17·8	0·21	—
	,,	,,	,,	27·4	0·48	—
	,,	July	,,	30·4	Not more than 0·42	—
	,,	Aug.	,,	32·4	0·31	—

The following tables record the results obtained in three experiments planned to study the seasonal variation in the vitamin potency of butter; in each of the experiments butters from known sources have been examined throughout the year.

Table V shows the results obtained for butters from Ayrshire cows on an English farm. Two samples were obtained each month, as the herd was divided into two groups receiving different diets.

TABLE V

Date of production of butter		International units per gram of butter.		Moisture-content of butter Per Cent.
		Vitamin *A*	Vitamin *D*	
April	1933	7·9	0·33	—
		5·0	0·35	—
August	1933	23·1	0·45	—
		19·8	0·45	—
November	1933	14·1	—	10·1
		16·3	—	17·2
December	1933	19·0	—	10·7
		14·9	—	8·7
January	1934	15·4	—	11·2
		16·6	—	12·3

TABLE V—*continued*

Date of production of butter		International units per gram of butter		Moisture-content of butter Per Cent.
		Vitamin *A*	Vitamin *D*	
February	1934	12·6	—	8·8
		12·8	—	7·7
March	1934	12·2	—	12·7
		7·7	—	7·7
April	1934	11·5	—	9·4
		8·2	—	10·4
May	1934	22·7	—	13·6
		21·2	—	15·9
June	1934	27·9	—	15·9
		26·7	—	21·2

The results set out in Table VI are for butters from a farm in Holland.

TABLE VI

Date of production of butter		International units per gram of butter		Moisture-content of butter Per Cent.
		Vitamin *A*	Vitamin *D*	
February	1935	12·0	0·1	10·1
March	„	14·0	Not more than 0·2	12·5
April	„	12·2	—	11·3
May	„	30·8	0·31	13·6
June	„	36·5	0·49	13·7
July	„	35·1	0·52	14·0
August	„	28·6	0·44	14·9
September	„	30·5	0·56	15·2
October	„	37·2	0·24	13·9
November	„	36·0	Not more than 0·17	14·0
December	„	27·0	0·13	12·8
January	1936	26·4	0·06	13·0

Table VII contains the results so far obtained on a series of creamery butters supplied by a Creamery in Ayrshire, Scotland.

TABLE VII

Date of production of butter		International units per gram of butter		Moisture-content of butter Per Cent.	Remarks
		Vitamin *A*	Vitamin *D*		
February	1936	14·8	0·215	13·8	
March	„	13·2	Not more than 0·08	11·9	Vitamin *D* estimated via unsaponifiable
April, I	„	15·3	„ „ 0·07	12·7	
April, II	„	15·3	„ „ 0·08	12·7	Last sample before cows went to grass
May	„	29·1	0·60	8·8	
June	„	29·5	0·99	13·5	
July	„	25·6	0·60	14·0	
August	„	26·0	0·50	9·0	
September	„	22·0	0·40	12·6	

DISCUSSION.—*Vitamin A*.—It has already been pointed out by Kon[6] that there is a wide variation in the vitamin *A* potency of butter, as shown by the published results of different authors; this, no doubt, is due to variations in source of the butters, combined with differences of technique in the biological methods employed. The average potency given by Coward and Morgan[4] for 17 samples of dairy butter is 60 units per gram, with a range of 26 to 200 units per gram. In contrast with these high figures are those published for Danish butters,[13] which show a range from 5 to 14 units per gram; Booth, Kon and Gillam[2] reported a range of 40 to 85 units per gram,—a value between those found by the Danish and English workers mentioned; whilst Treichler, Grimes and Fraps[12] give figures ranging from 1 to 70 units per gram in an experiment which involved "paired" feeding. The range of potency shown by the samples examined in the present investigation is from 5·0 to 38·6 units per gram; 75 samples in all were examined, and the average figure was 22·5 units per gram. The highest figure obtained by us is only about two-thirds that of the average potency reported by Coward and Morgan,[4] and is equal to the potency of winter butter found by Booth and Kon.[2]

Vitamin D.—In the paper mentioned above, Coward and Morgan[4] state that average butter contains 1·2 unit of vitamin *D* per gram with a range of 0·4 to 4·0 units per gram. Kon (1936) gave 0·7 unit per gram as his best value for pasture butter, and recently Campion, Henry and Kon[3] reported that they had obtained values between 0·15 and 0·88 unit per gram in butters produced during May and June under experimental conditions. These findings were confirmed by Bechtel and Hoppert,[1] who never expected a potency greater than 1 unit per gram of butter-fat. The results shown in this paper are in harmony with those of Kon, the average value being 0·36 unit per gram with a range of 0·06 to 0·99 unit per gram of butter.

The results of vitamin *A* and *D* potencies published by various workers have been summarised in Table VIII.

TABLE VIII

VITAMIN-POTENCY RESULTS PUBLISHED BY DIFFERENT WORKERS

		International units per gram	
		Vitamin *A*	Vitamin *D*
Campion, Henry and Kon	(1936)	—	0·15–0·88
Coward and Morgan	(1935)	26–200	0·4 –4·0
Kon and Booth	(1934)	40– 85	—
Kon	(1936)	—	0·7 (Summer)
Danish workers	(1934)	5– 14	—
Bechtel and Hoppert	(1936)	—	1·0
Treichler, Grimes and Fraps	(1935)	1– 70	—
Morgan and Pritchard	(1937)	5– 38·6	0·06–0·99

SEASONAL VARIATION IN THE VITAMIN-POTENCY OF BUTTER.—From our results, all the butters of known date of origin have been grouped, irrespective of source, according to the time of production, and the average assay of the butter-fat has been calculated for each month; where the moisture-content was not known, an average figure of 12·7 per cent. has been used. Table IX records the average values and the number of butters used in obtaining the assay for each month. The maximum value for vitamin *D* has been taken where the assay is not accurately known.

TABLE IX

THE AVERAGE VITAMIN *A* AND *D* POTENCY OF ALL THE BUTTER-FATS PRODUCED EACH MONTH

	Vitamin *A*		Vitamin *D*	
Month of production	No. of butters	Average value of fat in units per g.	No. of butters	Average value of fat in units per g.
January	3	22·0	1	0·07
February	4	14·6	2	0·18
March	4	13·4	2	0·16
April	6	11·3	3	0·24
May	4	29·8	2	0·51
June	4	35·9	4	0·80
July	2	35·3	4	0·60
August	4	27·8	3	0·53
September	2	30·6	2	0·56
October	3	30·4	1	0·28
November	3	25·8	1	0·20
December	3	22·9	1	0·15

In Fig. 1 the vitamin *A* and vitamin *D* contents of the butter-fats shown in Table IX have been plotted against the month. From the resulting graphs it is evident that the highest vitamin-potency is attained in summer and the lowest in late winter; for vitamin *A* this is in agreement with the conclusions of Gillam *et al.*,[5] based on spectroscopic examinations. The sharp rise in May obviously corresponds to the beginning of the grazing period.

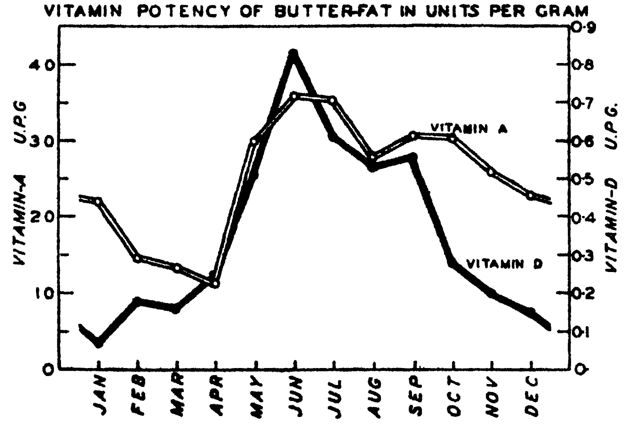

Fig. 1. Showing the relationship between vitamin-potency and month of production.

The average value for all the butters known to have been produced during the months from May to October is 27·2 units per gram of vitamin *A* and 0·49 unit per gram of vitamin *D*. For the winter period from November to April the values are 15·4 units per gram of vitamin *A* and 0·16 unit per gram of vitamin *D*. The values quoted here for vitamin *D* are thus lower than those quoted in the Medical Research Council's special report (1932),[8] which gives an average value of 1·0 unit per gram; this is higher than any assay obtained in the present series.

SUMMARY.—The vitamin *A* and *D* potency of many butters has been determined by biological assay.

The average vitamin *A* potency of 75 samples of butter has been found to be 22·5 units per gram.

The vitamin *D* potency has been determined in 39 samples, and the average figure is 0·36 unit per gram.

From a systematic study of samples of known origin and date of production a graph has been produced showing the fluctuation in potency throughout the year. The results obtained show that the lowest vitamin *A* potency, reached at the end of winter feeding, is 10 to 14 units per gram of butter-fat, and the highest, reached in June to July, is about 30 to 40 units per gram of butter-fat. The lowest vitamin *D* potency, during winter feeding, is from less than 0·1 to 0·3 unit per gram. During the summer, the values range from about 0·4 to about 1·0 unit per gram of butter-fat.

The average summer butter, in this series, has a potency of 27·2 units per gram of vitamin *A* and 0·49 unit per gram of vitamin *D*. The average butter produced in the months from November to April contained 15·4 units of vitamin *A* per gram and 0·16 unit per gram of vitamin *D*.

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The Determination of Cobalt. A new Method of Volumetric Determination, and a new Method for its Determination in Steel*

By B. S. EVANS, M.B.E., M.C., D.Sc., F.I.C.

GRAVIMETRIC.—The literature of the analytical chemistry of cobalt is extensive, complicated and many-sided. Few elements have more or more multifarious methods of determination to their credit; on the other hand, few have so many methods which are not quite good enough when one requires great accuracy. The electrolytic method beloved of text-books seems either not to remove all cobalt from solution or to give a contaminated deposit.[1] The phosphate precipitate obtained by Schoeller and Powell's method[2] leaves a certain amount of cobalt in solution for which a correction has to be made; precipitation, as sulphide, appears to be complete, but the problem of washing the precipitate is acute; water carries it through the filter, ammonium salt solutions dissolve appreciable amounts, alkali salt solutions are satisfactory but fatal to a gravimetric finish. The precipitation with α-nitroso-β-naphthol[35] appears to be complete and the precipitate can be washed; also, it has the merit of giving a separation from nickel; the difficulty here lies in the fact that it is (or was) apparently impossible to buy a reagent uncontaminated with iron. The finish of the determination is a further slight difficulty; doubts have been thrown (somewhat unnecessarily, I consider) on the accuracy of the conversion to Co_3O_4 on ignition.[3,4] On the other hand, one may convert the cobalt into $CoSO_4$ and weigh it as such, but here again there is the doubt whether it is possible to eliminate all excess sulphuric acid without at the same time decomposing a trace of the sulphate[4,5]. In my view, however, with careful work, both oxide and sulphate methods are capable of greater accuracy than has generally been assigned to them. Reduction to metal by ignition in a current of hydrogen is said to overcome the difficulty in both cases.[39] A method has also been published for obtaining the cobalt complex with α-nitroso-β-naphthol, free from the precipitant, and weighing it as such.[34]

Good results, both gravimetric and volumetric, appear to have been obtained by the 8-hydroxyquinoline method.[6,7] So many metals are precipitated by this reagent, however, that a rigorous separation of the cobalt is first required.

SEPARATION.—The separation of cobalt is in itself not an easy matter; it co-precipitates with stannic tin when the latter is thrown down by hydrogen sulphide in hydrochloric acid solution,[8] and with zinc when the precipitation is made in acetic acid solution.[9] In view of these facts and of the work published showing that iron and zinc both co-precipitate with copper sulphide in quite strongly acid solution,[10] there is at least a suspicion, in lack of positive evidence to the contrary, that co-precipitation of cobalt with sulphides is a thing to be guarded against.

Cobalt co-precipitates to a serious extent with metals of the third group thrown down with ammonia[11]. It, of course, follows nickel in most of its reactions. If cyanide is used at any stage for keeping cobalt from being co-precipitated in some reaction, there is danger that some at least of the cobalt will be converted into cobalticyanide, in which form not only is the cobalt difficult to recover, but the cobalticyanide itself gives precipitates with many metals in acid solution. One of the most difficult, and also one of the most important, metals to separate from cobalt is iron, and here the valuable α-nitroso-β-naphthol process, as hitherto applied, breaks down, for the reagent precipitates the iron as well as the cobalt.[12] In consequence of this, the usual procedure is to separate the cobalt from the iron group by precipitating the latter with zinc oxide, assuming that the cobalt is left entirely in solution. This point has been investigated by Hoffman,[13] who came to the conclusion that, although the method gives approximate separation, a certain amount of cobalt is always precipitated, and he accordingly gave a method for eliminating this error, but apart from the somewhat irksome restrictions in carrying out the precipitation, the method demands re-precipitation, which in steel analysis involves the solution and retreatment of the ferric hydroxide from 2 grams of steel. It is noteworthy that Hoffman followed up his investigation into the zinc oxide separation by a second paper a year later, giving a method for determining cobalt in steel in which this separation is not used at all, the iron being removed by ether extraction.[14]

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* Communication from the Research Department, Woolwich.

A useful method for the separation of cobalt by means of precipitation with phenyl-thiohydrazoic acid eliminates many metals, including the bulk of the iron, but not apparently nickel or the last few mg. of iron.[4] The dinitroso-resorcinol precipitation requires the removal of iron and copper.[15]

VOLUMETRIC.—Turning next to volumetric processes for the final determination of the separated cobalt, we have the choice of a large number of methods. Of these, some, depending on precipitation by 8-hydroxyquinoline, etc., appear, as mentioned above, to be capable of giving good results. The same seems to be true of certain electrometric methods[16]; these latter, however, need, of course, special apparatus and technique.

The attention of those in search of volumetric processes for cobalt has been largely centred on the fact that precipitated cobaltic hydroxide can be dissolved in a measured excess of a reducing agent and the excess of the latter titrated back. A number of methods of applying this reaction were examined by Willard and Hall,[4] who published many figures obtained by various modifications; many of these figures are excellent, but on the whole the variations seem to fall well outside those obtained by the method about to be described. The process has some distinct drawbacks, chiefly due to cobaltic hydroxide being a substance which does not dissolve readily in ordinary reducing agents. Willard and Hall's conclusions were that with potassium iodide the reaction was very slow, with acid ferrous sulphate an empirical factor had to be used, and with stannous or titanous chlorides air must be rigorously excluded. One of the most recent methods dependent on this principle is that of Sarver,[17] who reduces with ferrous sulphate in the alkaline liquid, air of course being excluded. I have tried many experiments with a view to making the cobaltic hydroxide method readily workable, but without obtaining consistently accurate results.

Other volumetric methods proposed are those based on titration of precipitated cobaltinitrite,[18,19,20] cobalt pyridine thiocyanate[21,22,23] or cobalt oxalate[24]. All these processes, like that using hydroxyquinoline, involve filtration as an integral part of the volumetric determination, and some need corrections for solubility. In another recent method cobalticyanide is titrated with silver nitrate, potassium chromate being used as an indicator.[25]

In face of all this wealth of processes it may seem waste of time putting forward yet another; there is, however, one possible method which has, for reasons to be stated later, been very much neglected of late years—the cyanide titration.

THE CYANIDE TITRATION.—Over and above the fact that most, if not all, reliable methods of volumetric determination of cobalt involve filtration and its attendant evils, the cyanide method has stood in need of investigation because it is perhaps the best method of determining nickel, and hence the analyst has been faced with a troublesome separation of nickel from cobalt when, as frequently happens, the two occur together. One outstanding paper has been published of recent years—that of Glasstone and Speakman[26]; the authors investigated the cyanide titration electrometrically and confirmed the theoretical basis of Rupp and Pfenning's method,[27] which assumes a Co: (CN) ratio of 1 : 5 at the end-point. Rupp and Pfenning's method involves running the solution of nickel and cobalt into the cyanide—a procedure which, though quite simple and straightforward when it is essential, is one that involves an additional dilution to a known volume, with a certain amount of waste of a possibly limited sample, and one instinctively avoids it where possible; in addition, the end-point obtained is apparently difficult to observe, and conditions as to alkalinity, amount of ammonium salts, etc., have to be somewhat carefully adjusted. The Rupp and Pfenning titration, of course, gives the sum of the nickel and cobalt, and to obtain a measure of the individual components Glasstone and Speakman were driven back on the cobaltic hydroxide method which has been criticised above. A full discussion of the theoretical aspect of the question is given in the paper referred to, and there is no point in repeating it here. The authors, however, dismiss their attempt to use the ordinary potassium cyanide—silver iodide titration for cobalt, with the statement that they found it impossible to get an end-point.

What actually happens is that, when one has titrated the liquid with potassium cyanide until it is clear, after a moment's stand it clouds again; the liquid can again be cleared with cyanide but it again clouds, this time more slowly, and so on, the recurrence of the clouding becoming more and more slow; in these circumstances it is obviously impossible to get an end-point. Apparently the lower cyanide of cobalt first formed withdraws cyanide from the soluble silver cyanide complex, itself forming a higher cyanide, silver iodide being precipitated. This process, in itself slow, naturally becomes slower as less and less cobalt remains to be converted.

Attempts to speed up the conversion were not encouraging; heating accelerated it considerably, but, as cyanide is very apt to react with ammonia and the titration has to be conducted in its presence, the liquid began to turn brown, owing to the decomposition of the cyanide, long before the cobalt was all converted. The first step necessary before one could add the excess of cyanide required for the conversion was to find some means of rendering the solution alkaline without using ammonia; sodium hydroxide was not satisfactory, as the precipitate formed did not readily dissolve in the cyanide; sodium carbonate was better but by no means perfect; sodium bicarbonate better still. Eventually I found that an excess of borax gives a pink precipitate which can be approximately titrated away with cyanide without using silver at all. It is necessary to run the borax solution in all at once; if it is added gradually a blue precipitate, which is not readily soluble in cyanide, tends to be formed.

A number of experiments were next tried to find out the best method of converting the cobalt to the higher cyanide; the requirements were these:—(*a*) complete conversion; (*b*) a stable end-product; (*c*) no loss of cyanide either by destruction or volatilisation.

Being at that time under the impression that cobalticyanide was the end-product to be aimed at, I attempted the conversion by adding a variety of oxidising agents as well as the excess cyanide; the figures obtained fell roughly into two groups:

(i) With mild oxidising agents, *e.g.* air bubbling even at boiling temperature, the consumption of cyanide was considerably less than that required for the $Co:(CN)_6$ ratio.

(ii) With more drastic treatment, *e.g.* boiling with hydrogen peroxide, the consumption of cyanide was much greater than that calculated and cyanide had obviously been destroyed.

On examination I found that the figures obtained with the milder treatments tended to approximate to those required for a $Co:(CN)_5$ ratio, which agrees with Glasstone and Speakman's finding; but the agreement was by no means perfect; even with the mildest treatment a decided excess of cyanide over that ratio had been used up, and a considerable increase in the severity of treatment did not increase this excess by very much. This is illustrated by the following figures:

Cobalt taken	0·0050 g.
No. of ml. KCN solution required for $Co:(CN)_5$	6·23 ml.
,, ,, ,, ,, ,, ,, ,, $Co:(CN)_6$	7·46 ,,
,, ,, ,, ,, ,, ,, air-bubbled for 5 minutes cold	6·40 ,,
,, ,, ,, ,, ,, ,, heated to boiling, removed from plate, air-bubbled 5 minutes	6·45 ,,

A search in the literature of the subject revealed the statement by Manchot and Herzog[28] that hydrogen peroxide is set free during the atmospheric oxidation of potassium cobaltocyanide. This gave an explanation of the anomalous results, and I then found that if the potassium iodide, which has in any case to be used as an indicator in the final titration, is added before the initial titration with cyanide, results agreeing closely with the $Co:(CN)_5$ ratio are obtained.

The following process was worked out:

PROPOSED VOLUMETRIC METHOD.—*Solutions Required.*

Potassium cyanide (standard): 16·8 g. of KCN with approx. 10 g. of NaOH made up to 3500 ml.

Silver nitrate (standard): 5·792 g. of pure $AgNO_3$ per litre.

Borax: saturated aqueous solution.

Potassium iodide: 4 per cent. aqueous solution.

Sodium carbonate: 10 per cent. aqueous solution.

Ammonium chloride: 20 per cent. aqueous solution.

Dilute ammonia (1 : 1).

The faintly acid solution containing the cobalt to be titrated is placed in a flask and diluted to about 100 ml., the flask is swirled round and 20 ml. of the borax solution are tipped in from a measuring cylinder; this should result in the formation of a pale pink precipitate in the liquid; 10 ml. of the potassium iodide solution are next added, and the mixture is titrated with the standard potassium cyanide solution until the precipitate has dissolved and the liquid is only slightly hazy. The volume of cyanide used, V, is read, and an excess is added, bringing the total to $(1{\cdot}3V + 5)$. The exact volume added does not matter so long as there is an excess, which is provided for by the formula. As the titration has to be continued from the same burette after a few minutes, and as cyanide burette taps are very apt to leak, it is advisable to stand a small beaker under the burette while the process is being continued. To the liquid in the flask, now containing an excess of cyanide, are next added 10 ml. of the sodium carbonate solution, and a rapid stream of air is drawn or forced through it for six minutes. This can conveniently be done by means of a wash-bottle attachment with the short arm connected with a filter-pump. It is advisable to adhere fairly closely to the time of aeration stated, as with less than five minutes the conversion seems to be incomplete, whilst with more than seven or eight, results tend gradually to be slightly high. At the end of the aeration the pump is disconnected, the attachment is rinsed in, and a mixture of 10 ml. of the dilute ammonia and 25 ml. of the ammonium chloride solution is added. The beaker, which has been standing under the cyanide burette, is rinsed into the flask, and the solution, which should be quite bright, is titrated with standard silver nitrate solution until it is permanently opalescent. Titration is now continued from the cyanide burette, drop by drop, with vigorous shaking until the liquid again becomes bright. This is the end-point, and the burette readings are noted. The burettes having been refilled, an amount of the standard cyanide 0·5 ml. less than the previous burette reading is run into the solution. This is again titrated to opalescence with the silver solution and again brought back to brightness with the cyanide; the two solutions are then run in alternately, drop by drop, until with the original amount of cyanide added the end-point is reached. The new silver reading gives the amount of silver solution required to balance the amount of cyanide used, the original one, that required for the excess cyanide; the difference between the two is a measure of the amount of cobalt combined with the cyanide; this number, multiplied by 0·803, gives the weight of cobalt in milligrams.

Experimental results were as follows:

TABLE I

Cobalt taken g.	Titration ml.	Cobalt found g.
0·05000	80·00—17·70=62·30	0·05001
0·02992	49·80—12·55=37·25	0·02992
0·02500	44·10—13·00=31·10	0·02498
0·02000	38·00—13·00=25·00	0·02006
0·01497	28·45— 9·80=18·65	0·01498
0·01000	24·55—12·15=12·40	0·00995
0·00500	11·85— 5·75= 6·10	0·00490
0·00200	10·70— 8·20= 2·50	0·00201

Titrations carried out on known mixtures of nickel and cobalt showed that, as might be expected, the figures for the two metals are merely additive; these results are given in Table II.

TABLE II

Cobalt taken g.	Nickel taken g.	Titration ml.	Titration calculated ml.
0·0300	0·0030	50·70−10·25=40·45	40·40
0·0240	0·0090	48·90−10·00=38·90	38·90
0·0180	0·0150	48·90−11·60=37·30	37·40
0·0120	0·0210	47·80−11·90=35·90	35·95
0·0060	0·0270	48·60−14·05=34·55	34·50
—	0·0330	46·00−12·95=33·05	33·00
Direct titration in ordinary way	0·0330	36·80− 3·75=33·05	33·00

The last two determinations show that the titration of nickel gives the same result by the process as by the ordinary cyanometric method. The factor for nickel is 0·0010.

Originally, 10 ml. of 20 per cent. sodium hydroxide solution were used, instead of the sodium carbonate added after the initial titration. This gave accurate figures with the higher amounts, but the results tended to be low with the lower amounts. On the other hand, when no alkali at all was used high results were obtained, presumably owing to slight decomposition of the excess cyanide.

TABLE III

Cobalt taken g.	Sodium hydroxide solution (20 per cent.) ml.	Sodium carbonate solution (10 per cent.) ml.	Cobalt recovered g.
0·0250	10	—	0·0249
0·0250	—	10	0·0250
0·0100	10	—	0·0095
0·0100	10	—	0·0099
0·0100	10	—	0·0094
0·0100	—	10	0·0100
0·0100	no alkali		0·0104

TITRATION OF NICKEL IN PRESENCE OF COBALT.—In view of the recently assumed industrial importance of electro-deposited nickel-cobalt alloys, it seemed worth while to try and find a reliable method for the volumetric determination of one or other constituent independently which, combined with the joint titration given above, would give a complete analysis of the alloy. Not having had very happy experience of the cobaltic hydroxide titration (*vide supra*), I turned my attention to the conversion of the cobalt into the very stable cobalticyanide form, followed by recovery of the nickel from its more unstable complex. This principle has been used before by Feigl and Kapulitzas,[30] who, however, add formaldehyde to remove the excess cyanide, thus rendering impossible a subsequent direct cyanide titration. The recovery of nickel from its cyanide complex is not quite so simple as at first sight appears. The complex is readily decomposed by acids, but the immediate result is the formation of an extremely insoluble white precipitate—apparently a nickel nickelocyanide analogous to Prussian blue; this precipitate resists all further attempts at decomposition. Prolonged boiling of the complex with a large excess of very faintly acid ammonium citrate effects decomposition, and the nickel can then be titrated; results, however, though approximately correct, seem to be invariably somewhat low; probably still a trace of the insoluble compound is formed. The following extremely simple procedure was found to give entirely satisfactory results:

The solution is made slightly ammoniacal, an excess of potassium cyanide (2–3 ml. of the saturated solution should be ample for an ordinary alloy) is added, followed by a few drops of hydrogen peroxide (20 vol.); the solution is then boiled for 5 minutes. The cobalt should now be entirely converted into the inert cobalticyanide, while the nickel remains principally as nickelocyanide; 20 ml. of ammonium chloride solution (20 per cent.) are added, and the liquid is boiled for a further 15 minutes. The flask is now removed from the plate and 10 ml. of dilute (1:1) ammonia followed by 10 ml. of hydrogen peroxide are added; the flask is replaced on the hot plate and boiled very gently for 10 minutes. This stage of the process is the only one which needs careful attention; it is necessary to dispel all the hydrogen peroxide, but, if the ammonia is boiled off too far, nickel cobalticyanide comes down as a white precipitate. Nickel cobalticyanide is not readily re-dissolved in a small excess of ammonia; if it has been precipitated the titration can still be performed, but it takes longer. The flask is now cooled, a few drops of citric acid solution (100 g. to 200 ml. of water) are added, followed by 10 ml. of dilute (1:1) ammonia and 10 ml. of potassium iodide solution (4 per cent.), and the solution is diluted to approximately 250–300 ml. with water. The titration is carried out as follows:—Standard potassium cyanide is run in until the blue colour of the solution is practically dispelled, then 1 to 2 ml. of the standard silver solution are added from the burette. This probably produces a turbidity, and in that case more cyanide is run in until the turbidity is dispelled and the solution is bright. If nickel cobalticyanide has been precipitated, it will still be visible at this stage, and if so, a few ml. excess of potassium cyanide solution must be added and the flask allowed to stand, with occasional shaking, until all solid particles are dissolved. In either case the turbidity is brought back by the addition of a little more silver nitrate and then just dispelled again by the addition of potassium cyanide, added drop by drop. The silver nitrate value of the total potassium cyanide added is found in exactly the same way as in the cobalt titration by adding nearly the full amount to the titrated liquid, titrating this away with silver nitrate, and then cautiously titrating alternately with the two solutions until the balance occurs when the full amount of potassium cyanide has been added.

The difference in ml. between the two volumes of standard silver nitrate solution thus obtained is equal to the weight in milligrams of nickel present.

The following experimental results were obtained by this method:

TABLE IV

Taken			
Nickel g.	Cobalt g.	Titration ml.	Nickel found g.
0·0300	0·0030	35·60 – 5·60 = 30·00	0·03000
0·0270	0·0060	36·00 – 9·00 = 27·00	0·02700
0·0240	0·0090	31·65 – 7·65 = 24·00	0·02400
0·0210	0·0120	24·40 – 3·50 = 20·90	0·02090
0·0180	0·0150	21·35 – 3·40 = 17·95	0·01795
0·0150	0·0180	17·70 – 2·80 = 14·90	0·01490
0·0120	0·0210	13·70 – 1·70 = 12·00	0·01200
0·0090	0·0240	12·50 – 3·45 = 9·05	0·00905
0·0060	0·0270	8·25 – 2·10 = 6·15	0·00615
0·0030	0·0300	4·50 – 1·50 = 3·00	0·00300

The complete process therefore for the determination of nickel and cobalt in a mixture of these two metals gives us two titration figures expressed in ml. of the silver nitrate solution

(i) combined nickel + cobalt titration = x ml.
(ii) nickel titration = y ml.

then:

$$\text{Cobalt} = (x - y)\ 0{\cdot}803 \text{ mg.}$$
$$\text{Nickel} = y \text{ mg.}$$

The method was tried on five electro-deposited alloys of nickel and cobalt supposedly free from other metals. Results were as follows:

TABLE V

Weight taken for each titration g.	Combined titration (ml. AgNO$_3$)	Nickel titration (ml. AgNO$_3$)	Cobalt found g.	Nickel found g.	Composition per cent.	
0·0320	34·05	22·90	0·00895	0·02290	Co	27·98
					Ni	71·58
						99·56
0·0320	34·45	20·75	0·01100	0·02075	Co	34·38
					Ni	64·85
						99·23
0·0320	35·45	17·20	0·01466	0·01720	Co	45·80
					Ni	53·73
						99·53
0·0320	36·15	14·00	0·01778	0·01400	Co	55·59
					Ni	43·76
						99·35
0·0320	38·75	4·80	0·02725	0·00480	Co	85·12
					Ni	14·98
						100·11

It must be clearly borne in mind that, before the cobalt titration can be carried out, other metals, especially iron, copper and zinc, must be eliminated.

SEPARATION OF COBALT FROM IRON, ETC.; DETERMINATION IN STEEL.—By far the most widely used method for the separation of cobalt from most metals appears to be its precipitation by α-nitroso-β-naphthol. It is especially unfortunate that iron is also precipitated by this reagent in view of the fact that this metal almost always accompanies cobalt, that many industrial alloys of cobalt also contain notable amounts of iron (*e.g.* cobalt steels), and that really reliable and simple methods of eliminating iron which do not involve filtration of large amounts of ferric hydroxide are conspicuously lacking (*vide supra*). The most usual way of removing the iron preliminary to determining cobalt in steel analysis is by zinc oxide separation. The objections to this method have been stated earlier (*vide supra*). Both the 8-hydroxyquinoline and the pyridine thiocyanate methods precipitate iron as well as cobalt. Many methods have been published which claim to effect the separation,[2,30,31,32,36] but all, or almost all, of these methods, granted that they are all that is claimed for them, suffer from the serious disadvantage (from the point of view of steel analysis) that it is the iron which is precipitated whilst the cobalt remains in solution.

The claim made for the process which follows is that the cobalt is precipitated substantially free from most metals, including iron, without any preliminary separation whatever.

The usual solvent used for α-nitroso-β-naphthol is acetic acid, and this solution, as has been said, precipitates iron as well as cobalt. The reagent is, however, soluble in a number of other liquids, and in syrupy phosphoric acid it gives a solution which, while still precipitating cobalt, copper and ferrous iron,[32] no longer precipitates ferric iron. The ordinary medium in which precipitation is effected is dilute hydrochloric acid. This may, however, be replaced by dilute nitric acid without ill effect so long as the nitric acid is free from oxides of nitrogen. This fact enables alloys to be readily brought into solution with the iron in the ferric condition without the introduction of possibly harmful reagents. One difficulty in the α-nitroso-β-naphthol precipitation has always been that the reagent itself is precipitated as well as the cobalt complex. This makes it difficult to know when an adequate excess of the precipitant has been added; the technique adopted in the process to be described overcomes to some extent this difficulty. A double precipitation has been adopted; this is principally due to the fact that the nitroso-naphthol precipitate is very bulky and difficult to wash, and, as a matter of fact, has always been the correct procedure where large amounts of metal (*e.g.* nickel) in solution have to be eliminated. Copper still precipitates with the cobalt and, as it reacts with cyanide, must be removed; this is achieved by a hydrogen sulphide precipitation before the second nitroso-naphthol precipitation; as pointed out earlier, there is the possibility that cobalt may tend to co-precipitate with copper sulphide. The amount of copper in steels, however, is generally so small that the co-precipitation may be ignored; with an alloy containing copper it will probably be desirable to re-precipitate the sulphide. Attempts were originally made to determine the cobalt gravimetrically. These were unsuccessful, as the results were invariably somewhat high; apparently it is difficult to remove all phosphoric acid from the precipitate, but in view of the success of the volumetric process, this question has lost its significance. The process finally worked out for the determination of cobalt in steel is as follows:

Determination of Cobalt in Steel.—The sample (5 g. for low amounts, less for higher) is dissolved in dilute nitric acid (sp.gr. 1·2) in the proportion of 75 ml. per 5 g.; the solution is boiled for 10 minutes and cooled, and about 0·5 g. of urea is added. The reagent solution, which should not be more than 2 or 3 days old, is prepared by placing the α-nitroso-β-naphthol in a small beaker, adding syrupy phosphoric acid in the proportion of 50 ml. to 3·5 g. of nitroso-naphthol, placing the mixture on the hot plate and stirring it with a thermometer until the temperature reaches 60° C., and finally cooling. The solution of the sample is diluted to about 100 ml., and the reagent solution is added, 1 or 2 ml. at a time, with subsequent stirring, a few seconds being allowed to elapse between additions during which stirring is continued. The following phenomena are observed: The liquid darkens, then a red turbidity, which increases as the additions continue, is produced, and after two or three additions a stable froth is formed and carries up the red precipitate. At a certain point, with continued addition and stirring, the precipitate suddenly begins to darken, the froth breaks or shows a tendency to break, and a black resin-like scum floats to the surface. This marks the presence of an excess of reagent, but it is advisable to add a final quantity of 3 to 4 ml.

The liquid is next diluted with about its own volume of 20 per cent. acetic acid and stirred, and about 3 ml. more of the reagent are run in (omission of this last precaution seems, for some reason, to lead to a tendency to slightly low results). The liquid is allowed to stand (cold) for about 25 minutes (not less than 20), with occasional stirring, and the precipitate is filtered off on paper and well washed with cold dilute nitric acid (5 per cent., prepared by diluting 20 per cent. nitric acid which has been boiled for 15 minutes).

The precipitate so obtained is dark coloured, probably nearly black, and very bulky, and may contain a good deal of water. The filter and its contents are transferred to a roomy platinum dish and placed on the plate to dry. (This is usually advisable, as quite a considerable amount of liquid may separate on heating.) When sufficiently dry the dish is placed in the muffle, and the filter is burnt off at not too high a temperature. If vanadium, molybdenum or tungsten (*vide infra*) is present, the residue is fused with fusion mixture, taken up with hot water, and filtered, the precipitate is washed with hot water, and the filter is replaced in the platinum dish and again burnt off; in the absence of these elements this step may be omitted. When completely burnt off the residue is fused with potassium bisulphate, heating being continued until potassium sulphate begins to crystallise as a scum on top of the melt. If an appreciable amount of cobalt is present, the melt will be dark blue when hot and pink when cold; in absence of copper, it may be dissolved in about 100 ml. of 5 per cent. nitric acid, the solution boiled, and cooled, and the second precipitation carried out forthwith, but with a steel it is safer to proceed as follows:

The melt is dissolved in water, and the solution is transferred to a beaker, hydrogen sulphide is passed, the liquid is heated to boiling, and the precipitate is allowed to settle, then filtered off, and washed with hot water. The filtrate is boiled until hydrogen sulphide has been dispelled, 25 ml. of the boiled-out, 20 per cent. nitric acid are added, and the liquid is boiled down to a volume of about 100 ml.

After cooling, the second precipitation is effected in exactly the same way as the first, but no urea is added. The resulting precipitate should be crimson lake in colour. It is allowed to settle, filtered off, and washed as before. It is desirable to test the filtrates of both this and the first precipitation for excess of reagent; this may be done by removing about 50 ml. of the filtrate (before washing), dividing it into equal parts, and adding about 0·2 mg. of cobalt to one of them. After standing for some time, the formation of the cobalt precipitate in one of them generally causes a distinct difference in appearance between the two parts. Too much stress must not be laid on this test; with the filtrate from the second precipitation it is almost invariably and immediately successful, but in the first precipitation the excess of the reagent seems itself to be mainly precipitated or destroyed.

After washing, the filter and precipitate are transferred, this time to a porcelain crucible. Platinum must not be used, as the subsequent solution of the cobaltic oxide in hydrochloric acid liberates chlorine; silica does not seem so satisfactory as porcelain. The filter will probably need drying again before ignition; it is then burnt off as before, care being taken to see that the burning off is complete and that no carbon particles remain. After ignition, the residue should be black; it may have white or blue patches, presumably due to phosphoric acid which has escaped removal.

When the residue is cool, about 10 ml. of strong hydrochloric acid are poured on, part of it being used to rinse down the sides. The crucible is then covered with a watch-glass and stood on a steam-bath. When the acid is hot a fairly vigorous reaction ensues, which should result in the residue dissolving completely to a blue solution. When this is achieved the cover-glass is removed and rinsed in with hot water, and the acid liquid is evaporated to dryness over steam. The sides of the crucible are rinsed down with about 15 drops of strong nitric acid, the solution is again evaporated to dryness, and the residue of cobalt nitrate (which should be dark red) is taken up with 2 drops of nitric acid and about 10 ml. of hot water; this should give a pink solution which is probably slightly hazy. The solution is transferred to a beaker and cooled; it may contain a very small trace of iron which must be removed, not because it is sufficient to influence the titration, but because it may cause a haze in the liquid and make the end-point difficult to observe.

The removal is effected by the addition to the cold liquid of a suspension of barium carbonate in water, added a few drops at a time until a trace of undissolved barium carbonate is floating in the solution as a semi-flocculent precipitate.* The precipitate, along with any trace of iron that was present, is filtered off, and the precipitate is washed with cold water. The filtrate is now ready for the addition of borax, and the remainder of the volumetric procedure is carried out as already described. Only one slight modification has to be introduced in this procedure because of the soluble barium salts produced by the barium carbonate treatment. When sodium carbonate is added after the initial titration, this of course precipitates the barium; therefore, after aeration and the subsequent addition of ammonia and ammonium chloride, the liquid is filtered and the precipitate is washed with cold water. The final titration is then proceeded with as usual. The trace of iron requiring removal by barium carbonate is so small that no appreciable amount of cobalt is carried down with it.

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* Great care must be taken to avoid any excess of barium carbonate, otherwise a little cobalt may be lost by adsorption (*vide infra*).

TABLE VI

Trials of this method were carried through with the following results:

Iron taken g.	Nickel taken g.	Copper taken g.	Cobalt taken g.	Titration ml. of $AgNO_3$ soln.	Cobalt found g.	Per cent. of cobalt added	Per cent. of cobalt found (corr. for blank)
5·00	0·050		Blank	3·40— 3·25= 0·15	0·00012*	—	—
5·00	0·050		0·0020	7·65— 5·10= 2·55	0·00205	0·0400	0·0386
5·00	0·050		0·0050	16·35—10·00= 6·35	0·00510	0·1000	0·0996
5·00	0·050		0·0100	24·90—12·70=12·20	0·00980	0·2000	0·1960
5·00	0·050		0·0250	38·85— 7·55=31·30	0·02513	0·5000	0·5002
5·00	0·050		0·0500	77·80—15·90=61·90	0·04972	1·0000	0·9920
5·00	0·050	0·010	0·0100	31·20—19·10=12·10	0·00972	0·2000	0·1920

* That this blank was really due to cobalt was shown by the colour of the hydrochloric acid extract of the residue.

The method was tried, without modification, on steel "W" of Messrs. Ridsdale's British Chemical Standards. The percentage composition of this steel as given in the certificate is:

C, 0·695; Si, 0·187; S, 0·075; P, 0·028; Mn, 0·101; Cr, 3·01; V, 0·791; W, 16·21; Co, 4·76; Ni, 0·44; As, 0·01; Cu, 0·058; Mo, 0·048.

As I was then unaware of the precipitation of vanadium, etc., by the reagent, the first precipitate was fused direct with bisulphate, the fusion with fusion mixture being omitted.

The very considerable amount of tungsten (16·21 per cent.) was ignored throughout, and was finally filtered off with the barium carbonate precipitate just before the titration was begun. The results obtained were as follows:

TABLE VII

Weight taken g.	Titration ml.	Cobalt Per Cent.
0·5000	47·20—18·70=28·50	4·58
0·5000	47·30—19·00=28·30	4·55
0·5000	43·75—15·30=28·45	4·57
0·5000	43·45—15·30=28·15	4·52

The cobalt figure, 4·76, given in the certificate is the mean of a large number of determinations by 19 independent referees using a great variety of methods; the individual figures given vary from 4·52 to 4·99. As I made no attempt to work up the barium carbonate precipitate (*vide infra*), it is very probable that my figures are slightly low.

Interference by Chromium, Vanadium, etc.—After completing the work so far described I came across the statement in Hillebrand and Lundell's text-book,[37] that bismuth, silver, chromium, zirconium, titanium, vanadium, tin, and nitric acid* also "interfere" (with the gravimetric determination of cobalt by precipitation with α-nitroso-β-naphthol). Time did not permit of an exhaustive examination of this question, but, in view of the use of chromium, vanadium, and titanium in alloy steels, it was necessary to ascertain the effect of these metals, at least, on the process.

As is proved by the figures given in this paper, nitric acid is entirely harmless if certain simple precautions are taken; further experiments showed that:

(*a*) Chromic salts do not seem to be precipitated by the reagent to any extent; a slight precipitation takes place, but this is presumably due to adsorption, and possibly also to the fact that

(*b*) Chromic acid appears to be precipitated.

(*c*) Vanadic acid is precipitated (vanadyl salts were not tried).

(*d*) Vanadic acid does not interfere with the cyanide titration.

In the process as applied to steel the chromium is left as chromic salt; the vanadium, on the other hand, is largely converted into vanadic acid; consequently, in the first precipitate, one has

(*a*) All the cobalt; (*b*) all the copper; (*c*) at least a great part, probably the whole, of the vanadium, molybdenum, tungsten, etc.; (*d*) a little chromium and iron.

Of these, the cobalt and copper have already been dealt with; the trace of chromium behaves in much the same way as a trace of iron, and is eliminated therewith; such of the vanadium, etc., as gets through into the titration liquid exerts no influence, and, in any case, vanadium, tungsten and molybdenum are removed by the fusion with fusion mixture.

An initial experiment (made before I realised the extent to which vanadium is precipitated) was carried out with a solution containing 1·452 g. of chromium and 0·700 g. of vanadium. This was divided into two equal portions, and 0·010 g. of cobalt was added to one of them. After adjustment of the nitric acid strength the two solutions were precipitated with the phosphoric acid—nitroso-naphthol reagent in the usual way; the precipitates obtained were burnt off in porcelain, and the residues were taken up with hydrochloric acid, thus proceeding direct to the latter part of the process without a second precipitation. A great deal of vanadic acid did not go into solution when the crucible was rinsed out, and was consequently filtered off with the barium carbonate precipitate. The titration behaved normally, but the result was somewhat low—0·0090 g. of cobalt in place of the 0·0100 g. taken. The barium carbonate precipitate on being worked up (*vide infra*) furnished a further 0·0005 g. which had been entangled in the undissolved vanadic acid, giving a total recovery of 0·0095 g.; the blank required 0·30 ml., which quantity was deducted from the titration figure. The lost 0·0005 g.

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* Lundell, Hoffman and Bright[38] say "Iron, copper, molybdenum, chromium, zirconium, titanium, vanadium, tin, and tungsten are also precipitated. Nitric acid interferes."

was probably not precipitated owing to an insufficient quantity of reagent having been used for so large an amount of vanadium.

The second experiment was carried out with smaller quantities of vanadium and chromium, but with addition of titanium; each solution contained 0·025 g. V, 0·037 g. Ti and 0·145 g. Cr, and 0·010 g. of cobalt was added to one of them. The process used was as for steel, but the first precipitate, after being burnt off, was fused with fusion mixture. The melt was taken up with water, and the precipitate was filtered off and washed with hot water. The precipitate was again burnt off and then fused with bisulphate, the resulting melt being treated like the ordinary bisulphate melt of the first precipitate (reprecipitation, etc.). Copper being absent, hydrogen sulphide was not used. The titration of the cobalt sample required 11·65 ml., and that of the blank, 0·15 ml.; the cobalt corresponding to the difference of these figures is 0·00924 g. There had therefore been a loss of 0·00076 g., or 0·95 ml. The barium carbonate precipitate was then worked up (*vide infra*), and the titration resulting was 0·70 ml., bringing the total cobalt recovered up to 0·00980 g. It would seem, therefore, that the trace of chromium (or vanadium?) left after the second precipitation tends to drag down a fraction of a milligram of cobalt in the barium carbonate precipitate.

It is clear that none of the three metals tested in any way prevents the precipitation of the cobalt, and the only form of interference shown was the removal of a trace in the barium carbonate precipitate. For ordinary purposes this trace can probably be neglected; for accurate work it can be recovered as follows:—The barium carbonate precipitate is burnt off in a platinum dish and fused with potassium bisulphate, the melt is taken up with 5 per cent. nitric acid, boiled and filtered, the filtrate is then treated with the nitroso-naphthol reagent in the same way as the solution of the bisulphate melt of the first precipitate in the ordinary process, and the determination is finished as usual.

In the above trial about a milligram of blackish residue was obtained on burning off this precipitate, and this dissolved in hydrochloric acid to give a blue solution; the hydrochloric acid solution of the "blank" residue was not blue, and the 0·15 ml. titration figure was probably an experimental error. The vanadium extracted in the alkali fusion of the first precipitates was titrated; that from the cobalt sample contained 0·0135 g., and that from the blank 0·0158 g., out of a total in each case of 0·0250 g. The loss seems to have occurred during burning off. I hope to investigate the vanadium question later, with a view to a possible method for determining vanadium in steel. Lack of time prevented further work being done on the separation of cobalt from chromium, vanadium, titanium, molybdenum, etc., but, as indicated above, there seems no reason to fear that precipitation will be incomplete or that alkali fusion will fail to remove the vanadium, molybdenum, etc.

It might be mentioned, in conclusion, that precipitation of cobalt in the usual way with an acetic solution of the nitroso-naphthol and with phosphoric acid added to the cobalt solution does not have the desired effect, iron being precipitated to a considerable extent; increase in the amount of phosphoric acid, with the object of holding the iron up completely, seems to prevent the complete precipitation of the cobalt. Several experiments carried out with the aim of preventing the reagent precipitating while allowing of the complete precipitation of the cobalt complex, by means of the addition of excess of acetic acid, acetone, etc., appeared to indicate that, under these conditions, the solubility of the cobalt complex is by no means negligible.

The cobalt solution used for these experiments was made up from a specially prepared sample of very pure electrolytic cobalt; the iron used was electrolytic iron of a high degree of purity; the nickel was a very pure sample of Mond nickel, which previous analysis had shown to contain 0·02 per cent. of cobalt. All reagents used were of analytical reagent quality except the α-nitroso-β-naphthol, which was old stock.

SUMMARY.—(*a*) A new volumetric method of determining cobalt has been described. This method closely resembles the ordinary nickel titration.

(*b*) A method has been described for titrating nickel in the presence of cobalt.

(*c*) A new method of separation of cobalt from all metals interfering with the volumetric procedure has been detailed.

(*d*) A preliminary survey of other metals precipitated by the reagent has been made, and their non-interference with the method has been demonstrated.

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The Precipitation of Metals by means of 8-Hydroxyquinoline (Oxine)

Part II. The Effect of *p*H on the Precipitation of Cadmium, Tungsten, and Uranium from Acetate Solutions

By H. RONALD FLECK, B.Sc., A.I.C.

In continuance of the work published in Part I of this series,[1] the *p*H range for complete precipitation of cadmium, tungsten, and uranium from acetate solutions, has been determined.

Minor variations of conditions may lead to inaccuracies in oxine determinations, and a description of the procedure used is therefore included in the present paper. Small departure in detail has been found on occasion to produce sticky and tarry precipitates which cannot be handled quantitatively.

A table showing the amounts of acid and alkali necessary to give approximately any required *p*H is also appended.

Procedure.—The neutral solution of the metal is diluted to the required volume, *i.e.* 110 ml. minus the volume of acid or alkali necessary to attain the desired *p*H; 25 ml. of 20 per cent. ammonium acetate solution, 10 ml. of 2 per cent. oxine in *N* acetic acid, and the required volume of acid or alkali are mixed in a separate beaker, heated to boiling, and added in a thin stream, with constant stirring, to the boiling solution. The beaker is covered and placed on a hot plate, and its contents are allowed to boil gently for exactly 5 minutes and then filtered through a sintered glass crucible (1.G.3 unless otherwise specified), and the filtrate is collected in a dry Buchner flask for the determination of *p*H. The precipitate is washed with 250 ml. of boiling water in small portions, and dried to constant weight.

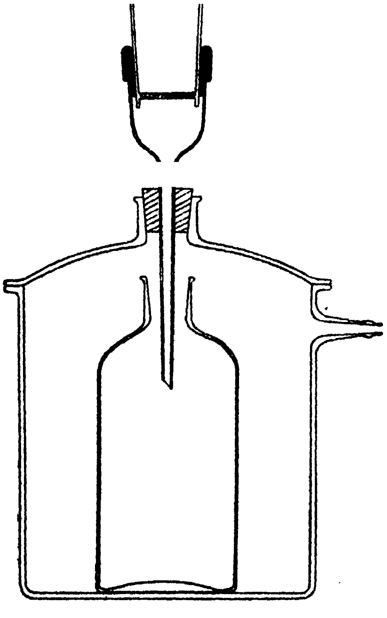

Fig. 1

For the volumetric determinations, 10-oz. stoppered bottles have been found best. The apparatus shown in Fig. 1 affords the simplest method of transferring the precipitate quantitatively to the bottle.

The complex is dissolved by running 50 ml. of hydrochloric acid (1:1) through the crucible and washing with 50 ml. of water, suction being applied at the side-tube. The stem is then washed with a little water, and the solution is ready for titration by the procedure of Fleck, Greenane and Ward.[2]

TABLE I

ACID AND ALKALI NECESSARY TO ATTAIN AN APPROXIMATE *p*H

Acid or alkali	Approximate *p*H
20 ml. glacial acetic acid	3·6
10 „ „ „ „	4·1
5 „ „ „ „	4·4
4 „ „ „ „	4·5
3 „ „ „ „	4·6
2 „ „ „ „	4·7
1 „ „ „ „	4·8
100 „ water only	4·9
5 „ *N* sodium hydroxide solution	5·6
10 „ „ „ „ „	6·3
15 „ „ „ „ „	7·4
20 „ „ „ „ „	8·3
30 „ „ „ „ „	8·9
40 „ „ „ „ „	9·4
50 „ „ „ „ „	9·8
60 „ „ „ „ „	11·6
80 „ „ „ „ „	12·3
100 „ „ „ „ „	13·2

These figures are intended only as a guide, since it is not possible to forecast accurately the *p*H which will be attained under the given conditions.

CADMIUM.—The solution used contained 14·204 g. of pure cadmium sulphate, $3CdSO_4.8H_2O$, per litre, which corresponds with 62·25 mg. of cadmium, with 222·0 mg. of $Cd(C_9H_6ON)_2$, and with 44·3 ml. of *N*/10 potassium bromide-bromate solution per 10 ml. of cadmium solution.

The solution was standardised both by precipitation as molybdate and by evaporation and ignition to $CdSO_4$.

10 ml. = 150·6 mg. of $CdMoO_4$ ≡ 62·25 mg. of Cd/10 ml.
25 „ = 288·7 „ „ $CdSO_4$ ≡ „ „ „

The weight of anhydrous oxine complex was calculated from the titre figure of 44·3 ml. of *N*/10 potassium bromide-bromate solution, since it is difficult to obtain the complex anhydrous, or even in a constant state of hydration. Precipitates dried at 100° C. for equal periods had the compositions:

(*a*) $Cd(C_9H_6ON)_2$, 0·75H_2O; (*b*) 1 H_2O; (*c*) 0·67 H_2O; (*d*) 0·6 H_2O; (*e*) 1·5 H_2O.

The results obtained for cadmium are given in Table II (see p. 380); 10 ml. of the cadmium solution were used for each determination.

Complete precipitation under the specified conditions takes place between *p*H 5·66 and 14·58, the horizontal portion of the curve (Fig. 2) extending over the range 5 ml. of *N* NaOH to 100 ml. of 5*N* NaOH.

TUNGSTEN.—The solution used contained 11·96 g. of $Na_2WO_4.2H_2O$ per litre. This was standardised by the lead tungstate and benzidine tungstate methods.

Weight of $PbWO_4$ from 25 ml. = 0·3749 g. ≡ 0·6652 per cent. of tungsten.
„ „ WO_3 „ „ „ (benzidine) = 0·2097 g. ≡ 0·6653 per cent. of tungsten.

Hence 10 ml. contain 66·52 mg. of tungsten ≡ 182·2 mg. of $WO_2(C_9H_6ON)_2$ ≡ 28·9 ml. of $N/10$ potassium bromide-bromate solution.

When freshly precipitated, the complex is soluble in hydrochloric acid, and the volumetric procedure is applicable, but when dried at 100° C. the precipitates are insoluble in conc. hydrochloric acid, and hence they were not titrated in this series. The complex after drying is only slowly soluble in boiling *aqua regia*, but dissolves in conc. sulphuric acid to give a purple solution (*cf.* molybdenum complex, Part I).[1]

TABLE II

*p*H	Complex mg.	$N/10$ KBr–$KBrO_3$ ml.	*p*H	Complex mg.	$N/10$ KBr–$KBrO_3$ mg.
3·58	—	—	8·47	222·0	44·30
4·13	—	—	8·95	222·0	44·30
4·40	—	—	9·45	222·0	44·30
4·43	—	—	10·25	222·0	44·30
4·50	40·1	8·0	11·15	222·0	44·30
4·53	155·7	31·05	12·00	222·0	44·30
4·55	217·8	43·40	12·91	222·0	44·30
5·66	222·0	44·30	14·00	222·0	44·30
6·09	222·0	44·30	14·58	222·0	44·30
7·23	222·0	44·30	14·75	185·4	36·95

The composition of the precipitate was checked[3] by ignition to WO_3 under pure oxalic acid.

1 g. complex = 0·4622 g. WO_3 = 36·5 per cent. of tungsten.
$WO_2(C_9H_6ON)_2$ requires 36·5 per cent. of tungsten.

The results obtained are shown in Table III and graphically in Fig. 2.

Complete precipitation, therefore, occurs from *p*H 4·95 to 5·65, which corresponds with the horizontal portion of the curve (Fig. 2) extending over the range 10 ml. of *N* acetic acid to 4 ml. of *N* sodium hydroxide solution.

In consequence of a suggestion that the *p*H range might be altered if the solutions were cooled before filtration, the experiments shown in Table IV were carried out. These show that the amount of precipitate is unchanged if the solution is cooled first.

TABLE III

*p*H	Complex mg.	*p*H	Complex mg.	*p*H	Complex mg.
3·20	—	4·50	161·0	6·25	126·0
3·35	—	4·62	168·0	6·43	99·0
3·40	—	4·82	180·6	6·62	48·0
3·46	—	4·95	182·2	6·85	6·0
3·52	6·0	5·08	182·2	7·05	—
3·60	19·5	5·25	182·2	7·50	—
3·70	48·0	5·45	182·2	8·21	—
3·82	90·0	5·65	182·2	8·60	—
4·15	132·0	5·80	174·0	8·87	—
4·45	157·0	6·06	142·6	9·76	—

TABLE IV

Acid or alkali	Hot filtration		Cold filtration	
	Complex mg.	*p*H	Complex mg.	*p*H
13 ml. of glacial acetic acid	127·8	4·03	127·6	4·04
10 ml. of *N* ,, ,, ,,	182·2	4·95	182·2	4·96
4 ml. of *N* sodium hydroxide solution	182·2	5·65	182·2	5·65
9 ml. of *N* ,, ,, ,,	126·0	6·25	123·0	6·28

URANIUM.—A solution was used containing 13·306 g. of uranium acetate made up to 1 litre, with the addition of 5 ml. of glacial acetic acid. This solution was standardised by precipitation as ammonium diuranate and ignition to U_3O_8

25 ml. = 0·2301 g. of U_3O_8 ≡ 0·7448 per cent. U.

Hence 10 ml. = 74·48 mg. of U ≡ 220·0 mg. of complex ≡ 37·6 ml. of *N*/10 KBr–$KBrO_3$.

The composition of the precipitated 8-hydroxyquinoline complex is given as $UO_2(C_9H_6ON)_2C_9H_7ON$, and this was checked[4] as follows: One g. was heated to 200° C. in a Wood's metal bath under slight suction. The brick-red complex changed colour to bright yellow and white crystals were deposited in the cooler part of the tube. The crystals had m.p. and mixed m.p. with 8-hydroxyquinoline of 74° C. The yellow residue was ignited under pure oxalic acid to U_3O_8.

Found U_3O_8 = 50·8 per cent.; $UO_2(C_9H_6ON)_2$ requires 50·3 per cent. of U_3O_8.

One g. of the brick-red complex was ignited under oxalic acid and gave U_3O_8=39·92 per cent., equivalent to 33·85 per cent. of uranium in the complex. (Theory, 33·85 per cent.)

The results for uranium, given in Table V and graphically in Fig. 2, show that complete precipitation extends over the range of *p*H 5·71 to 9·81, corresponding with 5 ml. of *N* NaOH to 30 ml. of *N* NaOH.

TABLE V.

*p*H	Complex mg.	*N*/10 $KBrO_3$–KBr ml.	*p*H	Complex mg.	*N*/10 $KBrO_3$–KBr ml.
2·89	—	—	8·54	219·9	37·60
4·20	—	—	8·95	220·0	37·60
4·45	—	—	9·06	220·0	37·60
4·52	75·0	12·80	9·09	220·0	37·60
4·65	156·7	26·75	9·44	219·9	37·60
4·70	183·5	31·30	9·58	220·0	37·60
4·84	205·0	35·05	9·81	220·0	37·60
5·05	211·5	36·10	10·14	217·0	37·05
5·71	220·0	37·60	10·26	202·7	34·60
6·31	220·0	37·60	10·34	168·7	28·80
6·67	220·0	37·60	10·40	120·0	20·50
7·22	220·0	37·60	10·60	33·7	5·75
7·78	219·9	37·60	10·80	—	—
8·09	220·0	37·60	11·68	—	—
8·44	219·8	37·60	13·46	—	—

Separations Based on the Foregoing Results.—On the basis of the results obtained the following separations should be possible:—Tungsten from cadmium, uranium from cadmium, uranium from tungsten, uranium from molybdenum, and other combinations of cadmium, tungsten and uranium from some of the metals given in Part I.

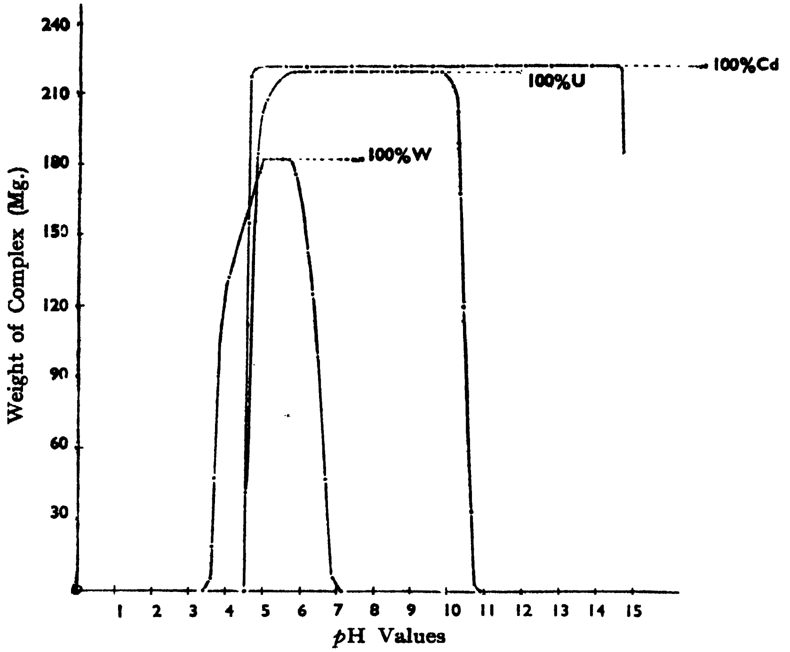

Fig. 2

Separation of Uranium and Molybdenum.—The aqueous solution (80 ml.) containing molybdenum, uranium and ammonium acetate (5 g.) was boiled, and 7 ml. of glacial acetic acid and 10 ml. of a 2 per cent. solution of oxine in N acetic acid were added. The mixture was boiled for 5 minutes, the molybdenum complex was filtered off, and the uranium complex was precipitated by the addition of a further 10 ml. of 2 per cent. oxine solution and 30 ml. of 5 N sodium hydroxide solution to the boiling solution. Each complex was then washed with 200 ml. of boiling water and dried to constant weight.

Table VI

Taken		Found		Error (per cent.)	
Uranium mg.	Molybdenum mg.	Uranium mg.	Molybdenum mg.	Uranium	Molybdenum
14·74	71·62	14·80	71·73	+0·41	+0·15
26·13	87·28	26·11	87·28	−0·07	0·00
42·55	57·91	42·47	57·88	−0·20	−0·05
67·00	55·95	66·93	56·08	−0·10	+0·24
86·10	23·50	85·83	23·45	−0·31	−0·22

In conclusion, I wish to thank Dr. A. M. Ward for his interest and helpful criticism during the course of this work.

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SIR JOHN CASS TECHNICAL INSTITUTE
JEWRY STREET, LONDON, E.C.3

Official Appointments

THE Minister of Health has approved the following appointments:

REGINALD FRANK WRIGHT as a Public Analyst for the County of East Sussex, in addition to S. A. Woodhead (March 12th, 1937).

WILLIAM WILDERS TAYLOR as a Public Analyst for the Borough of Grantham, in place of S. R. Trotman (retired) (March 12th, 1937).

HUBERT ALFRED PARKES as a Public Analyst for the Metropolitan Borough of Poplar, in addition to A. E. Parkes (March 12th, 1937).

The Minister of Agriculture has approved the following appointments:

R. F. BARKE as Agricultural Analyst for the County of Wilts and the County Borough of Bath, *vice* J. M. H. Munro (deceased).

A. N. LEATHER as Deputy Agricultural Analyst for the County Borough of Manchester.

D. W. MOIR as Deputy Agricultural Analyst for the County Borough of Croydon.

A. H. M. MUTER as Agricultural Analyst for the Holland and Kesteven Divisions of Lincolnshire, *vice* B. H. Gerrans (deceased).

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

FOOD-COLOURING PASTE CONTAINING LEAD

ON January 19th a manufacturing firm was summoned at the Kensington Petty Sessions for selling a colouring paste which was not of the nature, substance and quality demanded. The sample was taken in the course of delivery to a Kensington tradesman, and, when analysed by the Public Analyst (Mr. F. W. Edwards, F.I.C.), was found to be a bluish-red paste containing 540 parts per million of lead.

Dr. G. Roche Lynch, F.I.C., Senior Official Analyst to the Home Office, gave evidence to the effect that lead was a cumulative poison which tended to be deposited in the tissues, particularly in the bones. It had a special affinity for nervous tissue, and, if present in sufficient quantity, might damage that tissue. It was also a general cell poison and might affect other tissues, such as the kidney.

Under modern conditions it was the rule to find traces of lead in all the tissues, and it was always present in the urine. He had found quantities from 14·5 to 146 parts per million in human bones. Such quantities might do little harm so long as they were immobilised in the bone, but should this lead, under normal or pathological conditions, be mobilised, there was great danger of serious harm resulting. In his opinion, it was the absolute duty of those responsible for the purity of food to see that not more than the minimum of this poisonous metal reached the consumer.

The witness was in full accord with a statement in the Report of the Chief Medical Officer of the Ministry of Health for 1935, that "the only sound rule is to exclude all avoidable lead from food."

In his (Dr. Roche Lynch's) opinion the amount of lead in the sample before the Court was grossly excessive and avoidable, and should not be permitted. In a report published in THE ANALYST (1935, **60**, 547), the lowest quantity of lead found in the 12 food colouring materials examined was 6 p.p.m., and the highest was 40. Even assuming 40 p.p.m. to be a permissible limit, the amount in the sample was more than 13 times as much.

It might be argued that, as the quantity of colouring matter used on each occasion was extremely small, the amount of lead ingested from such a source would be negligible. Although this was true, he submitted that it was not so much a question of the quantity absorbed from an individual food as of the taking of small amounts of lead from a variety of sources, which, when added together, made a serious total. Therefore, in every case where the source of lead was avoidable it should be rigorously excluded.

The defendants entered a plea of guilty and were fined £5 and £10 costs.

ARTIFICIAL VINEGAR SOLD AS "TABLE VINEGAR"

ON January 27th a tradesman was summoned at Bow Street Police Court by the Westminster City Council for selling table vinegar not of the nature, substance and quality demanded.

Mr. Vernon Gattie, for the Westminster Council, said that the contention of the prosecution was that vinegar, whether sold as vinegar or table vinegar, must be malt or brewed vinegar.

Mr. F. W. Edwards, F.I.C., giving evidence in support of his certificate, said that the sample he analysed contained acetic acid, water and caramel, whereas he was of opinion that vinegar should essentially be a brewed article. The word "table" implied a superiority in that article. He then gave a brief outline of the process of making malt vinegar, and mentioned that brewed vinegars contained various products such as tartaric acid, aldehydes, esters, protein, and mineral matter, vitamins, etc., which gave them a characteristic aroma and flavour not present in artificial vinegars.

In cross-examination, Mr. Edwards said that he was aware that a few Public Analysts did not agree with his view, that no fluid in which the acetic acid was produced by processes other than fermentation should be sold as vinegar.

At the resumed hearing on February 18th Mr. Edwards submitted three references to chemical journals in which experiments showing that brewed vinegars contained vitamins were described.

Dr. C. Ainsworth Mitchell, F.I.C., said that he had been associated with the vinegar industry for over 35 years. He gave a short history of the manufacture of vinegar in this country, which, he stated, dated back to the early part of the seventeenth century. He would define vinegar as the product of the consecutive alcoholic and acetic acid fermentations of a saccharine solution derived from any source that would produce sugar. Brewed vinegar contained, in addition to acetic acid, various other products of fermentation which imparted flavour and character.

In cross-examination, Dr. Mitchell said that vinegar, in its original form, was sour wine (*vin aigre*), which was imported from France and sold in this country.

Acetic acid, made by processes other than fermentation, was used in the manufacture of pickles, its object being to remove the brine. The pickles were afterwards placed in malt vinegar, and he agreed that a substantial amount of the artificial acid would remain in them.

Mr. E. Hinks, B.Sc., F.I.C., Public Analyst for the County of Surrey, gave evidence that, in his opinion, vinegar should be the product of fermentation, and that a substance made from diluted acetic acid, coloured with caramel, was not vinegar, but should be described as artificial vinegar.

Evidence was then given by three well-known grocers and provision merchants to the effect that, in their opinion, table vinegar should be malt vinegar, and that a solution of acetic acid, water and colouring matter was not recognised in the trade as vinegar or table vinegar.

Dr. E. J. Parry, F.I.C., giving evidence for the defence, said that he had been concerned with the question of vinegar for about forty years. It was now possible to get acetic acid in such a state of purity that it was used for making vinegars of the type under discussion. There was a difference in flavour between this type of vinegar and malt vinegar. Acetic acid had steadily improved until they were getting an absolutely pure product, as they had been doing for twenty years at least. It had become so universally recognised over such a long period of time as vinegar—without any qualification—that he had definitely abandoned any view he might have had when dealing with the thoroughly impure wood vinegar. Malt vinegar was more expensive and a product of much nicer aroma than acetic acid vinegar.

The director of the firm who supplied the cask from which the sample in this case was taken said that his father had established the business in 1861, and that the firm had been selling this acetic acid vinegar ever since. It had been sold as "Table Vinegar" for about 45 years, but about five years ago they added the words "non-brewed" on the advice of their trading association.

Mr. W. Lincolne Sutton, F.I.C., Public Analyst for Norfolk and Suffolk, and Mr. A. J. Lickorish, F.I.C., Public Analyst for the City of London and the Metropolitan Boroughs of Lewisham and Stoke Newington, were of opinion that any preparation of acetic acid for dietetic purposes was vinegar. This implied that the acid was palatable and pure. Vinegar need not necessarily be brewed.

At the adjourned hearing on February 25th, Mr. Harold Murphy, K.C., in his speech for the defence, laid some stress upon the point that the sale was made in a jug, in a fried fish shop in a small street off St. Martin's Lane—a poor area—at a cost of only 1½d. for half-a-pint. He mentioned that two Bills, promoted by the Malt Vinegar Brewers' Association, had been before Parliament, but had been rejected. He submitted that the question for the consideration of the Magistrate was, whether it was established beyond all reasonable doubt that an ordinary member of the public going in and paying his 1½d. in a fried fish shop off St. Martin's Lane was getting, when he got this perfectly pure, innocuous substance, sold for forty years within the City of London, and sold without question, something not of the substance and quality demanded, so as to constitute a criminal offence.

The Chief Magistrate (Sir Rollo Graham-Campbell) gave his considered opinion on this case on the 17th March as follows:

This is a prosecution under Section 2 of the Food and Drugs (Adulteration) Act, 1928, the first Section of which is in the following terms: "No person shall sell to the prejudice of the purchaser any article of food or any drug which is not of the nature, or not of the substance, or not of the quality of the article demanded by the purchaser," and Sub-section (3) of that Section is as follows: "In any prosecution under this Section it shall be no defence to allege that the purchaser, having bought only for analysis, is not prejudiced." The facts with regard to the actual sale in the present case are not in dispute. The defendant keeps a fried fish shop at 8, New Street, in the City of Westminster, and on November 23rd, 1936, a

Mr. Gray (who was accompanied by Mr. Sutton, the Sampling Officer for the City of Westminster) went to the shop and asked for half-a-pint of table vinegar. Mr. Gray was served with half-a-pint of liquid in a jug, for which he paid 1½d., and the liquid was taken from a barrel which bore the words "Table Vinegar, non-brewed." Mr. Gray handed his purchase to Mr. Sutton, who dealt with it in accordance with the provisions of the Act, and handed one portion to the Public Analyst for the City of Westminster, who certified as follows: "I am of opinion that the said sample contained the foreign ingredient as under: 100 per centum of artificial vinegar, whereas table vinegar should consist of malt vinegar or other brewed vinegar," and I apprehend that the sole question which I have to determine is whether it is permissible to sell as vinegar a substance which is not malt vinegar and which is not brewed.

Before proceeding to consider this question, there are one or two preliminary matters which I should like to dispose of. Mr. Harold Murphy, in the course of his speech, seemed to lay some stress on the fact that the sale was in a jug. This appears to me to be quite immaterial. If you cannot sell this liquid as vinegar in a sealed bottle, you cannot, in my opinion, sell it as vinegar in a jug. Again, he laid some stress on the fact that the sale was at a fried fish shop in a small street off St. Martin's Lane, and that the purchaser for his purchase paid 1½d., whereas for a half-pint of malt vinegar he would have had to pay 2d., and Mr. Murphy submits that it has not been established beyond all reasonable doubt that an ordinary member of the public, not in Park Lane—but in a poor area—who goes into a fried fish shop and pays 1½d. for half-a-pint of vinegar is getting something different from that which he expects to get, and has a right to get; in other words, he has not been supplied with any article of food which is not of the substance or of the quality which he demanded. I cannot think that the place where the sale took place makes any difference at all. I think that vinegar has the same meaning in St. Martin's Lane as it has in the neighbourhood of Park Lane.

There is another matter to which I may refer, in passing. Mr. Murphy, in the course of his cross-examination of Dr. Mitchell, put questions for the purpose of eliciting the fact that Parliament had been invited, through private Bills promoted by the Malt Vinegar Association, to enact that the term "vinegar" should be only applied to malt vinegar, and that neither of those Bills became law, and in his speech he said that, although he fully appreciated that nothing Parliament does or does not do, unless its action crystallises in an Act of Parliament, has the smallest binding effect upon me, he does attach a little importance to the fact on the ground that it goes to establish the fact that the commodity in question is sold widely in great quantities in very large and important areas, without the smallest question, as vinegar. In my opinion, the fact that these Bills were introduced and rejected is quite immaterial.

On the other hand, I should like to make it clear that I am paying no attention to the passage from Dr. Hehner's article which was referred to by Mr. Gattie. He was, of course, clearly entitled to read that passage to Mr. Lickorish and ask him whether he agreed with it, but as Mr. Lickorish said he did not agree with the passage read from Dr. Hehner, the matter fell to the ground, and I dismissed it entirely from my mind.

The original form of vinegar was, no doubt, the *vin aigre*, a sour wine, but this kind of vinegar appears to have been comparatively little used in this country owing to the fact that England is not a wine-producing country, and it had to be imported and was expensive.

There can, I think, be no doubt that since the early part of the seventeenth century the commodity ordinarily sold in this country as vinegar was the product of fermentation, and that it was not until about the year 1890 that the fluid which we are now considering made its appearance on the market, although possibly there may have been isolated cases in which it was sold as vinegar as far back as

1860. Mr. Murphy says it is agreed on all sides that the substance sold by his client is innocuous and unadulterated, and is a perfectly harmless condiment which can properly be mixed with pickles supplied for human use or given to people who want to pour a little over their fried fish or their salad, but the real question is not whether this condiment is innocuous or unadulterated, but whether it can properly be sold as vinegar. Both vinegar which is the product of fermentation and the substance sold by Mr. Murphy's client are composed of acetic acid diluted with water in very much the same proportions, but the acetic acid in the one is produced in a way different from that in the other, and the vinegar produced by fermentation is not only produced in a way which does give the finished article a better aroma and flavour; it also contains other products of fermentation not present in the synthetic compound. ..

Bearing in mind the fact that for some three hundred years the substance sold as vinegar was the product of fermentation, and that it was admitted by the witnesses for the defence that it is produced in a way which undoubtedly gives it a better aroma and flavour, I have come to the conclusion that it is not permissible to sell as vinegar or table vinegar a substance which is not the product of fermentation.

I should hold as I have done apart from authority. The case of *Preston* v. *Jackson* (1928), 73, *Solicitors Journal*, page 712, was, however, cited to me. Whatever effect may or may not be given to that decision by the High Court, if the matter ever comes again to be argued before it, I cannot say, but I myself find it difficult to distinguish between that case and a case where I find, for the prosecution and against the defence, facts essentially the same as were left uncontradicted in that case.

The defendant was fined £5, and ordered to pay 25 guineas costs. Notice of appeal was given.

Ministry of Health

FIRST REPORT OF ADVISORY COMMITTEE ON NUTRITION*

THE Chairman of the Committee (which was appointed by the Minister of Health and the Secretary of State for Scotland jointly) is Lord Luke, and the membership includes a number of leading scientific experts including Professor Cathcart, Sir F. Gowland Hopkins, Professor E. Mellanby and Sir John Orr. The terms of reference are:—"To inquire into the facts, quantitative and qualitative, in relation to the diet of the people, and to report as to any changes therein which appear desirable in the light of modern advances in the knowledge of nutrition."

The Committee state that they believe this to be the first occasion in history that a comprehensive survey of the diet of a whole nation has been set on foot by any Government.

NUTRITION AND HEALTH.—In a brief review of the last quarter of a century, the Committee point to the great improvement in public health, including the lower incidence of deficiency diseases such as rickets, the steady improvement of the physique of school children and the fall in the general death rate, the infant mortality rate and the death rate from tuberculosis. The consumption per head of most foodstuffs, especially those of greatest nutritional value, has progressively increased, and that increase has continued particularly since the War, so that

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* Published by H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. April, 1937. Price 1s. net.

"the diet of the people is now more in conformity with physiological principles than it was in pre-war years." Much still remains to be done, however, before the general health and physique of the population reach an optimum level.

THE NATIONAL DIETARY.—In the light of statistics of national food consumption, the Report compares the quantities of the food available with the "optimum standards" of nutrition suggested by the Technical Commission of the League of Nations, with whose findings, subject to minor reservations, the Committee agree. They find that the national dietary contains sufficient energy-giving foods for the whole population, and that all, except a relatively small fraction of the population, are obtaining the full amount of calories they require.

MILK.—The average daily consumption of milk per head should, in the Committee's view, be about two pints for expectant and nursing mothers, from one to two pints for children, and not less than half-a-pint for the rest of the population; this is equivalent to about seven-eighths of a pint per day per head of the whole population. At the present time the consumption of milk in all forms is about half-a-pint per day per head—only 60 per cent. of the suggested amount, and much lower than that of many countries.

The Committee refute the view that skimmed milk "possesses little or no nutritive value"; they deplore the wastage of skimmed milk, and suggest that it would be most convenient for general use in the dried state.

OTHER FOODS.—The Committee recommend an increased consumption not only of fruit and green vegetables but also of potatoes—the latter in substitution for some of the sugar and highly milled cereals in ordinary diets. They also draw attention to the particular value of sea fish, as a source of protein and iodine and other mineral constituents; herring and mackerel are especially recommended as rich in vitamins *A* and *D*.

The Report contains four Appendixes:—I, Foodstuffs for Human Consumption in the United Kingdom (Home production and imports). II, The Nutritive Value of Milk, with tables of the approximate composition of milk and milk products. III, Extract from the Report on the Physiological Bases of Nutrition drawn up by the Technical Commission of the Health Committee of the League of Nations. IV, Conversion Factors for Meat, etc.

COMPARATIVE ANALYSES OF BACON AND HAM.—Analyses in Appendix IV were made for the Committee by Dr. R. A. McCance, and are contrasted with earlier analyses of Plimmer and of Atwater and Bryant.

	Per 100 g.		Energy value calories
	Protein	Fat	
McCance (1936)			
Tank-cured Wiltshire side (Danish)	14·3	37·1	404
Dry-cured Wiltshire side (British) ..	12·3	49·3	509
Midland cut (British shoulder belly) ..	10·5	61·1	611
York ham (British)	15·0	49·0	517
Plimmer (1918)			
Bacon side (type unspecified) ..	9·7	55·7	558
Ham	13·1	46·0	482
Atwater and Bryant (1906)			
Bacon, "edible portion"	10·5	64·8	646
Ham, smoked, "edible portion" ..	16·5	38·8	429

These values exclude the weight of bone, but include that of rind, the nutritive value of the rind being also included (whether rind was included in Atwater and Bryant's "edible portion" is uncertain).

Composition of Frozen Meat.—The following table shows the results of Dr. McCance's analyses of frozen meat:

Estimated Composition of Frozen Meat

	Veal			Beef				
	Source		Mean	Source				Mean
	New Zealand	Uruguay		Australia	Argentine	New Zealand	South Africa	
	g. per 100 g.	g. per 100 g.	g. per 100 g.	g. per 100 g.	g. per 100 g.	g. per 100 g.	g. per 100 g.	g. per 100 g.
Total nitrogen..	3·1	3·2	3·15	3·40	3·08	3·8	3·35	3·41
Purine nitrogen	0·057	0·045	0·051	0·052	0·053	0·056	0·048	0·052
Fat	2·66	4·6	3·63	6·65	12·0	1·8	8·5	7·24
Water	75·2	75·4	75·3	67·6	66·3	73·6	70·3	69·45
	mg. per 100 g.	mg. per 100 g.	mg. per 100 g.	mg. per 100 g.	mg. per 100 g.	mg. per 100 g.	mg. per 100 g.	mg. per 100 g.
Sodium ..	95	94	95	82	77	61	73	73
Potassium	380	375	378	365	338	445	338	396
Calcium	10·3	10·2	10·2	9·9	8·9	7·2	8·8	8·7
Magnesium	25	26·3	25·7	25·7	23	26	24·5	24·5
Iron ..	1·58	2·01	1·8	3·46	4·1	4·4	3·0	3·74
Copper ..	0·22	0·12	0·17	0·16	0·18	0·15	0·145	0·159
Phosphorus	210	190	200	197	205	200	188	198
Chlorine	94·5	101	98	89	70	57	77	73

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1935–36*

The Advisory Council of the Department of Scientific and Industrial Research, of which Lord Rutherford is the Chairman, directs attention, in their Annual Report, to important developments in the outlook of industry in this country. It is pointed out that the last five years have witnessed the fruition of the policy, adopted by several large industrial undertakings, of setting well-balanced teams of research workers, including chemists, physicists, engineers, and, where necessary, biologists, to solve a particular problem or to develop a new product.

Progress of the Research Associations.—The steady increase in the sum that industry is providing each year for the development of research associations is a good reason for taking an optimistic view of their future. In the last three years the sum has increased from £167,370 to £232,468, and in the same period the grants from the Department have increased from £68,212 to £107,451. In spite of various advances, however, the position of the Research Associations is not yet entirely satisfactory. The income of the associations might have been increased by a further £150,000 a year, of which only half had to be found by industry, if full advantage had been taken of the Department's offers.

Contact with Industry.—The Report cites a number of examples of various methods adopted to secure close contact and co-operation with industry. Thus a new Fire Testing Station at Elstree will be used for the study of the fire-resistance of full scale parts of buildings. A "Consultative Group," which brings the shipping industry into close contact with the Department's work on the transport and storage of food, has played an important part in the rapid development of the new trade in chilled beef with Australia and New Zealand, and in the application of improvements for transporting Empire fruit and dairy produce.

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* **H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1937. Price 3s. net.**

SAVINGS IN THE MILK INDUSTRY.—The Department is co-operating with the Milk Marketing Board on the purification of waste waters and effluents from milk depôts, creameries and condensed milk factories. Two different methods have been worked out whereby the polluting character of milk washings can be reduced by 97 to 99 per cent. The loss of milk, cream, whey, etc., can be reduced by nearly 3 million gallons a year, effecting a saving of £50,000 to the industry, and the loss of by-products can be reduced to about 2 per cent.

TRANSPORT AND STORAGE OF FOOD.—At the Low Temperature Station, Cambridge, the effects of radiation from radio-active substances in destroying bacteria are being studied in connection with the storage of meat.

Methods of storing eggs in different concentrations of carbon dioxide are being tested on a large scale. A high concentration of, say, 60 per cent., prevents attack by mould, and gives an excellent yolk but a very fluid white.

The manner in which the quality of pork and bacon is linked with the growth and diet of the pig is being studied. In the later growth of a pig, changes take place in the chemical composition of the muscular tissues. These start near the head and travel to the tail. This head-to-tail wave of growth explains why alterations in the rate of growth affect certain parts of the body more than others and influence the form and quality of the carcass. An ounce of cod-liver oil a day may be good for the living pigs, but causes the fat to become rancid in curing. Heavy exercise before slaughter, such as rapid walking for a quarter of a mile, makes the pigs' tissues more alkaline than they would have been had the pigs been rested for a day or two. This fact has been found to be of importance in dry salt curing.

STALE BREAD.—Exhaustive investigations carried out by the Flour Millers Research Association have shown that bread made in the best possible way from the best possible flour will leave little to be desired in the matter of keeping quality. Such bread will retain its edibility for ten or twelve days, whereas bread improperly made from poor flour may become most unappetising and almost uneatable in two or three days. Many other factors contributing to keeping quality have been investigated. The results of this work suggest strongly that if more attention were paid to commercially controllable factors promoting good keeping quality of bread, the serious problem of stale bread would lose some at least of its importance.

The report points out, however, that this important commercial aspect of bread staling is not true staling. This is caused by a change in the form of the starch in the bread from its natural form, occurring at high temperatures, to its natural form at low temperatures. Keeping quality is independent of this in true staling, except that if true staling could be prevented, the bread would probably always keep well. Retaining bread at a relatively high temperature is a sure way of preventing true staling, but this is not easy to carry out in commercial practice, on account of increased mould-growth at high temperatures.

ANAESTHETICS AND STATIC ELECTRIFICATION.—An investigation has been begun at the National Physical Laboratory on the production of static electrification in operating theatres in hospitals. Some of the anaesthetics used are of an explosive character, and the possibility of electrostatic charges and the risk of ignition by sparking cannot be neglected.

STATIC ELECTRIFICATION IN DRY CLEANING WORKS.—At the request of the Home Office a preliminary examination has been undertaken of the risk of ignition by sparks due to static electrification in dry-cleaning works. Some of the liquids used in dry cleaning produce an ignitable vapour when mixed with air, and explosion may result if the conditions of operation allow the generation of appreciable electrostatic charges.

MEASUREMENT OF RADIUM RADIATIONS.—The strength of the radiations from a specially designed radium unit, with which various radium "skin distances" can be obtained, have been measured in a water "phantom," a celluloid vessel containing water and giving the same scattering and absorption effects as a human body. Means have been developed for accurately measuring and controlling tissue-dosage. Another investigation is in progress in connection with the weak radiations which may reach distant parts of a patient's body during treatment. These radiations, it is believed, may be of importance in "constitutional effects" of radium treatment, *e.g.* blood changes and general health. The method used is to measure the electricity produced (ionisation) in air gaps in a laminated celluloid model of the body.

The improved apparatus for investigating artificial radio-activity is being used in a search for new radio elements of very short life whose existence is suspected. Particular attention is being given to those elements that occur in the human body.

REPORTS OF RESEARCH ASSOCIATIONS.—A summary review is given of the work carried out under the various research associations of the Department during the year.

Reports of the individual associations have also been published [*cf.* National Physical Laboratory (ANALYST, 1936, **61**, 478), Building Research Board (*Id.*, 1937, **62**, 303), Food Investigation Board (*Id.*, 1936, 759), Atmospheric Pollution (*Id.*, 257), and Water Pollution (*Id.*, 1936, 33, 546)].

Medicine Stamp Duties

REPORT OF THE SELECT COMMITTEE*

A SELECT Committee was appointed on November 11th, 1936, to consider the duties of excise chargeable under the Medicines Stamp Act, 1802, the Stamp Act, 1804, and the Medicine Stamp Act, 1812, and any enactment amending those Acts, and to report thereon, and make such recommendations for the alteration of those duties or otherwise as they think fit, with a view to reforming the law thereto. The Report has now been issued, and some of the main points are outlined in the following summary:

The Medicine Stamp Act of 1812, on which the present practice is based, repealed the Schedule of the Act of 1804, and substituted another (which still remains in force), containing the names of 550 preparations which were specifically made liable to duty, including "all artificial Mineral Waters and all Waters impregnated with . . . Carbonic Acid Gas . . . etc." The general charge on all articles not specifically named was continued, together with the schedule of exemptions, which included drugs vended, without the addition of any other drug or ingredient, by a duly qualified chemist, and known, admitted and approved remedies.

The present position may be summarised for practical purposes as follows:—All preparations (defined in the Schedule) to be used as medicines which are:—(*a*) secret or claimed to be such; or (*b*) proprietary or claimed to be such; or (*c*) held out or recommended as beneficial for the prevention, cure or relief of any human ailment—are liable to duty.

ANOMALIES.—A large number of products, not strictly medicines, are widely advertised for the relief, cure or prevention of some human ailment (*e.g.* tonic foods, beverages, appliançes, such as deaf aids and trusses, meat extracts, cereals, bread, and mustard).

A further anomaly, the abolition of which is recommended, is that whereas a preparation is liable to duty if it refers to an ailment name, it is free from liability if the reference is made only to an organ or part of the body (*e.g.* backache and kidney pills are liable; back and kidney pills are not).

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* Ordered by the House of Commons to be printed, February 18th, 1937. Published by H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1937. Price 3d. net.

Numerous "single drugs" sold under fancy names have successfully claimed exemption. As the result of a High Court judgment in 1903, and of a further decision in 1932 (*Attorney-General* v. *Lewis and Burrows, Ltd.*, 1932, 1 K.B., 538), the present position is that qualified chemists may sell unstamped, as "known, admitted and approved remedies," all remedies which are not secret or proprietary, and that this exemption may be successfully claimed where a formula in accordance with a standard book of reference is printed on the label and proprietary rights are disclaimed.

Mineral Waters.—By the Act of 1812 all artificial mineral water impregnated with . . . carbonic acid gas . . . and all compositions . . . for making . . . the said waters were specifically liable to duty. In 1833 this item was repealed, but medicinal waters or compositions for making them continued to pay duty until 1878, when, by a judicial decision, it was held that the earlier repeal operated as an exemption from duty. Since then all salines have escaped duty, even though held out to the public as medicines.

Another class of preparations which the Committee are of opinion should be made liable to duty consists of medicines usually labelled with a prescription number and advertised "to compete with" or be "equivalent to" well-known proprietary medicines.

CONTROL.—The terms of reference were interpreted to preclude any departure from the fiscal aspect of the question, but the Committee mention the fact that strong opinions were expressed by certain witnesses to the effect that people (largely the poorer and less well-educated) spend more money than they can afford on remedies of little or no efficacy, with an accompanying indirect danger to health as a result of their not seeking medical advice. Although there is reason to believe that matters are not so bad as they were, the Committee are strongly of opinion that the appeal to fear, which is the underlying motive of large numbers of advertisements, is psychologically harmful.

RECOMMENDATIONS.—The Committee make the following recommendations:

(1) That the Acts of 1802, 1804, 1812, Section 2 of the Finance Act, 1927, and all other existing legislation on the subject of Medicine Stamp Duties be repealed.

(2) That, subject to the exemptions mentioned below, "preparations or substances of any sort, including medicines, medicaments, medicated articles, drugs, herbs, fumigants, inhalants, disinfectants, antiseptics, soaps, tooth pastes, tooth powders, mouth washes, medicated wines, natural or artificial mineral waters or compositions for making such waters, confectionery, toilet preparations and cosmetics to be used or applied externally, internally or otherwise, as medicines or medicaments, which are recommended, held out, or advertised either directly or indirectly . . . for the prevention, cure or relief of any human ailment, defect, disorder, condition or habit, or for the treatment of any part of the human body, or for the protection or maintenance of bodily health, should be liable to a duty based on the retail selling price."

(3) That the present scale of duties should be revised . . .

[The rate of duty suggested ranges from ½d. to 1d. for articles not exceeding 6d., and 1d. for every 6d. or part of 6d. over 6d. If it were decided to adopt an *ad valorem* percentage duty, the Committee would recommend a rate of 16⅔ per cent., *i.e.* 2d. in the 1s.]

(4) That the Excise Licence of 5s. per annum be continued as heretofore.

(5) That exemption be granted to

(*a*) All medicines, etc., recommended and sold solely and exclusively to registered members of the medical and dental professions;

(*b*) all preparations, etc., supplied to registered medical or dental practitioners for use in the discharge of their professional duties, also all preparations, etc., supplied to registered pharmacists or registered medical or dental practitioners for use in dispensing as a component part of medicines prescribed by such practitioners;

(*c*) all medicines, etc., exported for use or consumption abroad; and
(*d*) all British spa waters consumed only at the place of origin.

The Committee would urge consideration of the propriety of taxing foods and certain appliances, beverages (alcoholic and otherwise) and other preparations widely advertised as possessing properties beneficial for health. Moreover, if it is found difficult to distinguish between cosmetics which claim to be remedial and those which do not, the taxation of all cosmetics might receive consideration.

Should control of the trade in medicines and appliances be deemed desirable, for the protection of the public, the Committee believe that the best method of achieving this would be by a system of examination and registration of all advertised medicines and appliances.

National Bureau of Standards

RE-DETERMINATION OF THE ATOMIC WEIGHT OF ALUMINIUM*

ALL recent determinations of the atomic weight of aluminium have been made by analysis of aluminium halides (T. W. Richards and H. Krepelka, *J. Amer. Chem. Soc.*, 1920, **42**, 2221; H. Krepelka, *Id.*, 1924, **46**, 1343; H. Krepelka and J. Nickolic, *Chem. Listy*, 1925, **19**, 158), and consequently depend on the purity of the halide and on the atomic weights of the silver and of the halogen involved.

In this re-determination, weighed portions of the metal were converted into the hydroxide and sulphate, respectively. These were then heated until converted into Al_2O_3, which was finally ignited at 1200° to 1300° C. By this procedure the atomic weight is related directly to that of oxygen. Analyses showed that the metal contained only very small amounts of impurities and disclosed no gases in the highly ignited oxide. Appropriate corrections were made for the small amounts of impurities, and special precautions were taken to prevent absorption of moisture by the ignited oxide during weighing.

According to Krepelka's work (*loc. cit.*) the atomic weight of aluminium lies between 26·972 and 26·978, according to Krepelka and Nickolic's work it lies between 26·970 and 26·976, and according to the present work it lies between 26·972 and 26·976. Since three different methods were employed in obtaining these values, it is suggested that the atomic weight of aluminium might properly be given in the International Atomic Weights to three decimal places somewhere between the limits 26·972 and 26·976.

Aston's work (*Nature*, 1936, **137**, 613) with the mass-spectrograph indicates that aluminium has no isotopes and that the mass of Al is 26·9909 (O^{16}=16·0000). This value, stated to be only provisional, when corrected to the chemist's scale by using the conversion factor 1·00020, to take into account the heavier isotopes of oxygen, becomes 26·9855. This leaves a discrepancy of approximately 0·01 between the chemically determined atomic weight and that obtained by the use of the mass-spectrograph. Spectrochemical tests showed that the alumina obtained in the present work contained less than 0·001 per cent. of boron, and no significant amounts of the alkali or alkaline earth metals. The special tests that were made for silicon and beryllium showed that no significant error could have been introduced by those elements. Hence the conclusion is drawn that it is most unlikely that the average positive error of 0·7 mg., required to explain the discrepancy, could have been made in determining the amount of aluminium oxide.

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* U.S. Department of Commerce. Research Paper R.P. 957. By J. I. Hoffman and G. E. F. Lundell. Pp. 18, 1937. U.S. Government Printing Office, Washington. Price 5 cents.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Amino Acids in Staple Foods. I. Wheat (*Triticum vulgare*). F. A. Csonka. (*J. Biol. Chem.*, 1937, **118**, 147–153.)—The individual amino acid-content was found to vary with different varieties of wheat. The varieties of wheat having a high nitrogen-content contained protein of a better quality than that present in wheat having a low nitrogen-content. The protein of whole wheat flour was found to have a nutritive value comparable with that of casein. Several indispensable amino acids were determined, but only trytophane was conspicuously low in concentration.

The following table shows the protein quality of three varieties of wheat as indicated by the relationship between amino acids and total nitrogen-content. The results are expressed in mg. of amino acid per g. of total nitrogen:

Wheat	Cystine	Tryptophane	Tyrosine	Arginine	Histidine	Lysine
Marquis	81	28	262	154	85	456
Tenmarq	65	26	173	146	43	475
Fulhio	67	34	217	152	34	373
Casein, for comparison	20	130	405	236	156	475

The nitrogen-content is still a convenient guide to the quantity of protein present, but, when there is malnutrition pointing to amino acid deficiency, a knowledge of the amino acid composition will indicate a remedy. A diet in which wheat is the only source of protein is liable to be deficient in trytophane. S. G. S.

Bromine in Flours and Wheats. R. P. Ibanez. (*Pamphlet*, Argentina, 1936, pp. 1–12.)—The following method, which gives results higher than those obtained by the method in which the organic material is removed by calcination, is recommended. Ten g. of finely powdered bread, or 10 g. of flour, are treated in a 200-ml. conical flask with 50 ml. of 90 to 95 per cent. alcohol and 2 ml. of a 10 per cent. solution of sodium or potassium hydroxide. The flask is weighed and heated to boiling-point on a water-bath or a metal gauze, with shaking; it is then allowed to stand and its contents again boiled. The alcohol lost by evaporation is replaced, the liquid is allowed to stand for a moment, and the clear liquid is decanted. Twenty-six ml. of the liquid (corresponding to 5 g. of bread or flour, allowing for the expansion of the hot alcohol) is evaporated in a 50- to 60-ml. porcelain crucible, and the residue is ignited at dull red heat, cooled, treated with 5 to 8 drops of a 10 per cent. sodium hydroxide solution, and ignited again at dull red heat until the ash is almost white; the operation takes no longer than 15 minutes. The ash is cooled and dissolved in 10 ml. of water, the solution is centrifuged to remove the remaining small particles of carbon, and the Denigés-Chelles reaction is applied to 5 ml. in a test-tube. Five drops of a 10 per cent. solution of potassium chromate and 1 ml. of pure sulphuric acid are added; the test-tube is allowed to stand for 15 minutes in water at 15° to 20° C., and treated with 1 ml. of the reagent (prepared by mixing 100 ml. of a 5 per cent. by vol. sulphuric acid with 10 ml. of a 0·1 per cent. solution of fuchsin) and 1 ml. of chloroform washed with water. The liquid is mixed in the tube closed with a rubber stopper, or, better, in a 2·5 × 20 cm. tube, in which it can be shaken without inverting the tube. The tube is left to stand, with occasional shaking, until the colour of the chloroform solution becomes no deeper, and a colorimetric comparison is made by one of the usual methods.

Doughs are prepared for examination by grinding 5 g. of the dried, but not charred, material with a few ml. of 90 to 95 per cent. alcohol in a mortar, transferring the mixture to a conical flask, washing the mortar 3 or 4 times with alcohol (the total volume of alcohol should be about 25 ml.), rendering the liquid alkaline with 1 ml. of 10 per cent. sodium hydroxide solution, heating it on a water-bath, and cooling, decanting and evaporating it in a crucible; two further extractions with 15 or 20 ml. of alcohol are carried out, and the solutions are evaporated in the same crucible. The procedure is then continued as described above. Wheats to be examined should be finely ground in a mill.

All the wheats examined contained combined bromine in quantities varying with the origin and quality of the wheat. The following are some of the results obtained:

Variety of wheat	Bromine g. per kg.
Ground Pergamino	0·0075
,, ,, (another mixture)	0·0070
,, Santa Fé	0·0055
,, ,, ,, (another mixture)	0·0050
,, v. Sinvalocho	0·0035
,, v. Mentana	0·0048
,, v. Palantelen	0·0010
,, v. Taganrot	0·0020
Candeal (ordinary)	0·0010

All the flours contained 0·003 to 0·004 g. of bromine per kg., with the exception of two varieties (Casilda, Santa Fé), which contained 0·0055 g. per kg. All the varieties of bread analysed contained quantities of bromine equivalent to those introduced in the flours and in the common salt used in their manufacture. It is concluded that wheats contain appreciable quantities of bromine and that a systematic study is needed to establish normal limits and to enable the method to be used for the detection of adulteration. E. M. P.

Refractometric Determination of Fat in Chocolate. J. Stanley. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 132–136.)—The rapid refractometric test described is intended primarily for works use. For chocolate of all types the results compare well with those obtained by the official (A.O.A.C.) method (in 20 determinations the maximum difference was 0·3 per cent.), and work is in progress on cocoa and cocoa shell to make the test applicable to these products, since at present they give low results. The solvents used must have refractive indices differing from that of cocoa butter to an extent consistent with accuracy; they must be cheap, good solvents for cocoa butter, and odourless, non-inflammable and innocuous to health. The following solvents answered the requirements:—tricresyl phosphate, n_D^{40} 1·5486, b.p. 420° C.; dibutyl phthalate, n_D^{40} 1·4855, b.p. 340° C., and diethyl phthalate, n_D^{40} 1·4948, b.p. 295° C. Twenty g. of the sample and 20 g. of tricresyl phosphate are weighed in a lipped beaker on a balance sensitive to 0·05 g. The mixture is left in a warm place (not over 75° C. for chocolate or 40° C. for milk chocolate), stirred until melted, left for 10 minutes, stirred again and filtered, and the Abbé refractometer reading is taken between 35° and 45° C., the exact temperature being noted. The percentage of fat is found from the following tables:

Cocoa butter per 10 g. of solvent	Refraction		
	35° C.	40° C.	45° C.
0·000	1·55039	1·54841	1·54659
0·250	1·54772	1·54563	1·54380
0·500	1·54498	1·54283	1·54115
0·750	1·54243	1·54031	1·53823
1·000	1·53892	1·53774	1·53593
1·250	1·53765	1·53533	1·53343
1·500	1·53547	1·53336	1·53167
1·750	1·53348	1·53150	1·52940
2·000	1·53146	1·52950	1·52700
2·250	1·52943	1·52738	1·52548
2·500	1·52774	1·52560	1·52400
2·750	1·52613	1·52445	1·52213
3·000	1·52434	1·52223	1·52049
3·250	1·52283	1·52076	1·51900
3·500	1·52148	1·51953	1·51778
3·750	1·52026	1·51814	1·51649
4·000	1·51856	1·51695	1·51524
4·250	1·51740	1·51540	1·51380
4·500	1·51649	1·51444	1·51253
4·750	1·51515	1·51307	1·51130
5·000	1·51358	1·51177	1·50997
5·250	1·51261	1·51081	1·50921
5·500	1·51185	1·50960	1·50819
5·750	1·51049	1·50906	1·50723
6·000	1·50967	1·50775	1·50619
6·500	1·50825	1·50615	1·50448
7·500	1·50495	1·50309	1·50110
8·500	1·50196	1·50014	1·49828
9·500	1·49950	1·49772	1·49570
10·000	1·49804	1·49627	1·49450

The concentration of cocoa butter is expressed as g. of fat per 10·000 g. of solvent.

The zero point for the solvent is obtained by making a blank test without the fat, and the difference between this figure and that given in the table is the correction to be used. It seldom exceeds a few units in the fourth decimal place. If a butyrorefractometer is used, dibutyl phthalate must be used as solvent, and in this case only half the weight of solvent is taken, and the mixture of solvent and sample must not be warmed above 50° C. In order to use the curves given in the paper the reading should be taken at 48° C. The small amounts of lecithin used in chocolate products do not interfere with the accuracy of the test.

D. G. H.

Iron-content of Grapes and Wine. J. Byrne, L. G. Saywell and W. V. Cruess. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 83–84.)—The iron-content of the juice of California grapes ranged from 23 to 1·5 p.p.m., depending on the degree of contamination with dust or soil. The iron-content markedly decreased during fermentation in iron-free vessels, *e.g.* from an average of 9·0 p.p.m. to an average of 1·8 p.p.m. Addition of sulphur dioxide before fermentation did not affect the decrease in iron during fermentation. The average iron-content of wines made commercially was approximately three times that of wines made in the laboratory in glass, suggesting solution of iron by the juice and wine from iron equipment. The determinations of iron were made by the colorimetric method of Saywell and Cunningham (*cf.* Abstract, p. 413). S. G. C.

Oil from the Seeds of *Solanum Xanthocarpum*. M. P. Gupta and S. Dutt. (*J. Indian Chem. Soc.*, 1936, 13, 613–618.)—*Solanum Xanthocarpum* is an important plant in Hindu medicine, being known as Bhatkatya in Hindi and Kanta-Kari in Sanskrit and Bengali. It is described in Dymock's *Pharmacographica Indica*, 1891, 2, 557, and in Basu and Kirtakar's *Indian Medicinal Plants*, 1918, 2, 896. The fruits examined contained 20·71 per cent. of dry seeds, 4·62 of pericarp and 74·67 per cent. of moisture. The powdered seeds were extracted with benzene and yielded 19 per cent. of a greenish-yellow oil which did not contain nitrogen or sulphur. The oil had the following characteristics:—Sp.gr. 27°/4°, 0·9240; $[\alpha]_D^{32}$, −1·35 in chloroform; thickened at −11° C.; saponification value, 182·5; iodine value, 124·3; Hehner value, 94·9; acetyl value, 40·4; acid value, 70·78; unsaponifiable matter, 1·2 per cent. The mixed fatty acids were separated by Twitchell's method into 16·62 per cent. of saturated and 83·38 of unsaturated acids, together with a small quantity of a resinous acid which accounted for the high mean molecular equivalent of the mixed acids (322·7). The saturated acids had iodine value 4·24 and mean molecular equivalent 285, and the unsaturated acids had iodine value 129·7 and mean molecular equivalent 279·8. The unsaturated acids, which showed a green fluorescence, were examined by the method of Jamieson and Baugham (ANALYST, 1920, 45, 303) by preparing the bromine addition products. The saturated acids were converted into the methyl esters and fractionally distilled. The composition of the oil was calculated as oleic acid, 42·93; linolic acid, 36·18; palmitic acid, 5·37; stearic acid, 9·77; arachidic acid (?), 0·35, and unsaponifiable matter, 1·2 per cent. The unsaponifiable matter was distilled and repeatedly crystallised from alcohol and two fractions of white crystals were obtained, one melting at 122° C. with previous shrinking at 92° C., and the other at 142–143° C., with no shrinkage before melting. They gave the various colour reactions of the sterol and were optically active. D. G. H.

Determination of Small Quantities of 2-Naphthylamine, Aniline and *o*-Toluidine in Certain Food Dyes. O. L. Evenson, J. A. Kime and S. S. Forrest. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 74–75.)—Small amounts of aniline and *o*-toluidine produce a strong yellow colour with calcium hypochlorite in alkaline solution, but only a faint colour in acid solution; 2-naphthylamine, on the other hand, gives a much stronger yellow colour in acid than in alkaline solution. The authors propose to determine the constituents colorimetrically in mixtures of small amounts of naphthylamine and aniline, or naphthylamine and toluidine, by first measuring the colour yielded by naphthylamine and hypochlorite in acid solution and then measuring the colour given when the solution is made alkaline. For accurate results, however, it is necessary for both constituents to be present in the standard comparison solution in approximately the same concentration as in the unknown solution, so that preliminary tests are required. Moreover, the quantities of calcium hypochlorite and alkali need careful regulation to ensure the full development of colour. The methods, for working details of which the original paper should be consulted, are applied to an acid aqueous extract of the intermediates from a benzene solution of the dye. S. G. C.

Resin and Volatile Oil in Cubebs. J. F. Clevenger. (*J. Assoc. Off. Agr. Chem.*, **1937**, **20**, 140–141.)—Approximately 10 per cent. of the analyses made of importations of cubebs into New York during the past five years indicated the presence of spurious fruits, in some instances to the extent of 50 per cent. Tables are given showing the yields of resin and volatile oil and the physical and chemical characteristics of the latter for authentic and adulterated cubebs. The results given were obtained by the method outlined in *Methods of Analysis*, 1935, p. 450 (*Assoc. Off. Agr. Chem.*), which has been adopted as tentative for the evaluation of ginger. The amount of resin found in authentic cubebs varied from 6·44 to 8·47 per cent., and in adulterated samples from 6·58 to 7·71 per cent. The yield of volatile oil from authentic cubebs varied from 12·5 to 20·0 ml. per 100 g., and from the adulterated samples from 10·3 to 17·0 ml. per 100 g. The following are the ranges of the characteristics of the volatile oil, the figures in brackets being the corresponding figures obtained from adulterated samples:—Sp.gr. at 25/25° C., 0·911 to 0·919 (0·879 to 0·910); optical rotation at 25° C., −19·7 to −46·0 (−17·3 to +22·5); n_D^{20}, 1·492 to 1·498 (1·476 to 1·492); acid value, 0·35 to 1·0 (0·5 to 1·8); ester value, 1·0 to 10·7 (3·6 to 5·4). Adulteration of cubebs is therefore clearly indicated by the physical constants of the volatile oil.

A. O. J.

Glucovanillin and a Colour Reaction for Vanillin. W. V. Thorpe and R. T. Williams. (*J. Chem. Soc.*, 1937, 494.)—*Glucovanillin.*—β-Glucovanillin is prepared by the condensation of vanillin and β-penta-acetyl glucose, as in the phenol condensation by the Helferich and Schmitz-Hillebrecht method (*Ber.*, **1933**, **66**, 378). An acetyl derivative is first formed (*cf.* Fischer and Raske, *Ber.*, **1909**, **42**, 1465), and this is hydrolysed by sodium methoxide in methyl alcohol (*cf.* Bergmann and Heimhold, *J. Chem. Soc.*, **1936**, 505), and β-glucovanillin is recrystallised from methyl alcohol. Constants are given.

Colour reaction of vanillin.—A stable purple colour (or precipitate with concentrated solutions) is obtained on boiling 1 ml. of an aqueous solution of vanillin with 2 drops of Millon's reagent. The reaction is given by a 0·002 per cent. vanillin solution. In very dilute solutions the mixture must stand for a few minutes to develop the maximum colour. With excess of reagent no colour is obtained. The reaction appears to be specific for the vanillin group, as out of 63 phenols examined (including eugenol, isoeugenol, guaiacol, and protocatechuic aldehyde and acid) only vanillin and vanillic acid gave the colour immediately. It is given after longer boiling by acetylvanillin, β-glucovanillin and potassium glucurovanillate. 5-Nitrovanillin gives no reaction. With *excess* of reagent, isoeugenol gives a purple colour which changes to brown. A very transient purple, which changes to deep red, is given by *p*-aminophenol. The reaction is not obtained with the separated or paired constituents of Millon's reagent. E. B. D.

Identification of Barbiturates with Millon's Reagent. M. Paget and Tilly. (*J. Pharm. Chim.*, 1937, **129**, 222–223.)—Millon's reagent should be prepared by the method of Denigès in the 1930 edition of his *Manuel de Chim. Analytique.* A solution of 0·05 g. of the substance in 4 ml. of acetone is treated with 5 drops of Millon's reagent. A white precipitate, soluble on heating for 4 to 6 minutes and then re-precipitated, indicates *veronal*; insoluble, on heating for 10 to 15 minutes, becoming grey, *dial.* White turbidity, increasing with shaking and heating, but dissolving with the simultaneous appearance of a slate-grey colour in 15 to 25 minutes, indicates *prominal.* Turbidity, dissolving on shaking and warming, with appearance of a grey precipitate in 20 to 30 minutes, indicates *evipan*; solution of the turbidity (increased by shaking) in 8 to 10 minutes, with appearance of grey colour after about another 11 minutes, *rutonal.* If no precipitate is formed with Millon's reagent, used as described above, 0·05 g. of the substance to be tested is dissolved in 4 ml. of 95 per cent. alcohol and 5 drops of Millon's reagent are added. A yellowish-white precipitate becoming yellow on warming, and white on the addition of a drop of conc. hydrochloric acid, insoluble in 10 ml. of cold hydrochloric acid, but soluble on warming, indicates *evipan.* A white precipitate, insoluble on shaking or on heating, but soluble in 10 ml. of hot hydrochloric acid, indicates *gardenal.* White turbidity, insoluble on shaking or heating, forming a precipitate with the first drop of hydrochloric acid, soluble in 10 ml. of the hot acid to an amber solution—*phanodorm.* Turbidity, soluble on warming, precipitating as above with hydrochloric acid, and soluble on heating to form a colourless solution—*soneryl.* No turbidity in the cold or on heating, but a precipitate with hydrochloric acid soluble in less than 10 ml. of acid, indicates *narcosol.* D. G. H.

Determination of Soluble Carbohydrates in Tobacco. C. Pyriki. (*Z. Unters. Lebensm.*, 1937, **73**, 196–199.)—The content of soluble carbohydrates is an index of the quality of Eastern tobaccos, the content increasing with improving quality. The author recommends the following methods for the various determinations:—The reducing capacity is determined by the gravimetric method of Meissl (König, *Chemie der menschlichen Nahrungs- und Genussmittel*, 1910, III, Part I, p. 430), and the quantities of sugars (as invert sugar) are read from the corresponding tables. The extract is prepared by heating 5 g. of powdered tobacco with a little calcium carbonate and 100 ml. of hot water in a 150-ml. flask, on a water-bath for half-an-hour, with occasional shaking. The contents of the flask are then cooled, made up to the mark and filtered, and the filtrate is used for the following determinations:—(i) *Total reducing power of the extract.* (*a*) *Before hydrolysis.*—Fifteen ml. of the extract (0·5 g. of tobacco) are treated with 25 ml. each of Fehling solutions I and II, and made up to 100 ml. The liquid is boiled for 2 minutes and cooled by the addition of 100 ml. of water. The cuprous oxide is collected in an Allihn tube, washed with hot water until the washings are neutral, dried with alcohol and ether, and ignited to cupric oxide, which is weighed. The corresponding weight of invert sugar, from Meissl's tables, multiplied by 200, gives the percentage content of reducing matter in the tobacco.

(*b*) *After hydrolysis.*—Fifteen ml. of the extract are heated for 2 hours on a boiling water-bath with 10 ml. of distilled water and 2·5 ml. of 25 per cent. hydrochloric acid in a 100-ml. round-bottomed flask, after which the liquid is cooled and neutralised with caustic soda solution. The contents of the flask are transferred to a conical flask, made up to 50 ml., and treated with 25 ml. of Fehling solutions I and II, the procedure after this being as under 1(*a*).

(ii) *Determination of the soluble carbohydrates.*—To 100 ml. of the extract (3·3333 g. of tobacco) in a 150-ml. flask are added 10 or 11 ml. of basic lead acetate solution, and the liquid is made up to 150 ml., and after about 10 minutes filtered through a pleated paper. Ninety ml. of the clear filtrate (2 g. of tobacco) are pipetted into a 100-ml. flask, treated with 2·5 to 3·0 ml. of a saturated sodium sulphate solution, and made up to 100 ml. The lead sulphate is filtered off after about 15 minutes, and the clear neutral filtrate is used for the following determinations. (The greater part of the dextrin is precipitated by the lead acetate; for its determination see below.)

(*a*) *Monosaccharides.*—To 25 ml. of the liquid (0·5 g. of tobacco) in a 300-ml. conical flask are added 25 ml. each of Fehling solutions I and II, the volume is made up to 100 ml., and the reduction is carried out as described under (i*a*). The corresponding weight of invert sugar, multiplied by 200, gives the percentage content of monosaccharides (glucose and fructose), plus the small content of maltose. The quantity of cupric oxide due to the maltose can be calculated from the results of the determination after hydrolysis, and the quantity of monosaccharides can thus be determined.

(*b*) *Disaccharides.*—Twenty-five ml. of the liquid are heated, with frequent shaking, for 2 hours on the water-bath, with 2·5 ml. of 25 per cent. hydrochloric acid. The contents of the flask are cooled, neutralised with caustic soda solution, made up to 50 ml. and filtered. Forty ml. (0·4 g. of tobacco) are used for the reduction. The quantity of soluble sugars is given as invert sugar per cent. The difference between the results of (ii*a*) and (ii*b*) gives the content of hydrolysable materials; this figure, multiplied by 0·95, gives the result as a percentage of sucrose. If the content of sucrose, apart from maltose, is required, a mixture of 25 ml. of the liquid, 12·5 ml. of water, and 2·5 ml. of hydrochloric acid (sp.gr. 1·19) is heated at 67° to 70° C. for 5 minutes in a 50-ml. flask, with frequent shaking. The liquid is cooled, made up to 50 ml. and filtered, and 40 ml. of the filtrate are reduced in a 300-ml. conical flask with 10 ml. of water and 25 ml. each of Fehling solutions I and II. The risk of tobacco acids causing hydrolysis during heating may be avoided by neutralising with calcium carbonate. For the determination of dextrin the sugars are removed from a quantity of tobacco by extraction with alcohol, and an aqueous extract made from the residue is hydrolysed by boiling for 6 hours with hydrochloric acid. After neutralisation the sugar is determined as glucose, and the amount, multiplied by 0·90, gives the quantity of dextrin. Schmuck has classed the non-carbohydrate reducing materials in tobacco among the polyphenols. Their quantity can be calculated from the difference between the results of (i*a*) and (ii*a*) or, better, from the difference between the results of (i*b*) and (ii*b*). For the chemical evaluation of the quality of the tobacco it is sufficient to know the total reducing power of the extract after hydrolysis and the total sugar content. E. M. P.

Biochemical

Curdling of Milk. A Study of the Curdling Enzyme. N. L. Söhngen, K. T. Weringa, and A. Pasveer. (*Rec. Trav. Chim. Pays. Bas.*, 1937, **56**, 280–299.)—The action of the curdling enzyme (rennet) on casein has been studied by using viscometric methods for determining the velocity of reaction. It was found that the velocity of the reaction depended on the ratio of casein to enzyme and was reduced by increasing the relative amount of casein present. The reaction velocity was also directly proportional to the hydrogen-ion concentration, and the increased velocity at higher *p*H values was probably due to the alteration of the state of the protein particle making it more accessible to the enzyme. It was also found that the velocity was reduced as the swelling of the protein particle increased, and rapid action took place when the particle was dehydrated. The high reaction velocity obtained when the enzyme acted on calcium caseinate was due to the fact that such a sol was less viscous than the corresponding sodium sol, and therefore more easily attacked. S. G. S.

Toxicological and Forensic

Fixation of the Time of Administration in Cases of Chronic Arsenic Poisoning. L. Van Itallie. (*J. Pharm. Chim.*, 1937, **25**, 97–101.)—It is known that arsenic absorbed by the system is removed partly in the hair, and that this is a gradual process and begins about 15 days after the arsenic has been taken. If, therefore, the rate of growth of the hair is known, a knowledge of the distance between the root and the point at which the arsenic is found will provide an indication of the date of administration. According to the literature, and also the author's measurements, 1·5 cm. per month is a reliable growth-figure for both male and female hairs. Allowance must be made for the normal arsenic-content of the hair, which the author's earlier work has shown to be 0·01 to 0·03 mg. per 100 g. of hair. There is reason to believe that the rate of elimination of arsenic via the hair is proportional to the concentration of arsenic absorbed by the system, and that the amount found in the hair may be small at first, and subsequently increase to a maximum and fall off again. Two examples of the application of the method are cited:—(1) A woman (59 years of age) developed arsenical poisoning in 1934, arsenic being found in the hair, nails and urine; generalised polyneuritis and melanosis were apparent. In March, 1935, she left the clinic, an improvement being noted, but a reaction for arsenic was obtained from 190 mg. of nails in September, 1935, and early in 1936 the above symptoms re-appeared in an aggravated state, and had become even more acute by May, 1936; the toe-nails contained 4·3 mg. of arsenic (as As) per 100 g. (2·67 mg. per 100 g. from the finger-nails). The arsenic-contents of 6, 7 and 7 cm. of hair, starting from the distal end, were 1·96, 1·31 and 0·47 mg. per 100 g., respectively, and these figures are in line with the history of the case, assuming the normal rate of growth (*vide supra*). (2) The arsenic-contents of portions of hair 1·5, 8, 8, and 21 cm. in length, starting from the root end, were 0·142, 0·86, 1·815, and 0·27 mg. per 100 g. of hair, corresponding with periods of 5, 11, 17, and 32 months, respectively, since the rate of growth in this case was 1·3 cm. per month. It was thence concluded that poisoning occurred over 18 months before the examination was made, and that 3 years later complete elimination of the arsenic taken had not occurred. J. G.

Detection of Blood on Firearms and Ammunition. A. Brüning. (*Chem. Ztg.*, 1937, **21**, 228–229.)—When a shot is fired at close range (as may occur in murder and suicide), blood stains and particles of tissue can often be found in and on the barrel of the weapon used, and their identification may be forensically important. In the case reported, red-coloured particles could be seen in the barrel, and, after being removed and cleaned from dirt and grease with petroleum spirit, they were at first considered to be blood particles, their unusual colour being ascribed to the conversion of the haemoglobin into the carbon monoxide compound by the gases of the explosion. Owing to the small amount of material the oxidase test was omitted and Riegler's reagent (alkaline hydrazine solution) caused gradual decolorisation, but not the usual change given by blood. When a spectroscopic examination was made, a strong absorption was obtained in the position typical of blood, but careful examination showed that, although the bands were deceptively similar to those given by blood, they were really different. Ultimately the red particles were identified as particles of lacquer coloured with a dyestuff of the eosin type. They had originated from the lacquer covering of the "oil-proof" ammunition, and may be expected to occur when such ammunition is used; hence a similar uncertainty may arise in other cases. S. G. S.

Bacteriological

Determination of Mould in Cream or Butter. J. D. Wildman. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 93–100.)—In the microscopical method for the determination of mould in butter, preliminary experiments showed that removal of fat is unnecessary and that a 0·75 per cent. solution of carob gum or of tragacanth containing 2 per cent. of formaldehyde as preservative affords the best suspending medium. The gum solution should be allowed to stand until a clear solution can be decanted from the cellular débris. One g. of butter, weighed in a spoon-shaped measure, is transferred to a beaker by pouring over the inverted measure a portion of a 7-ml. quantity of hot gum solution, the remainder being used to rinse out the measure. The mixture is then stirred until the fat globules are 0·1 to 0·2 mm. in diameter, a portion is mounted on a mould-counting slide, and the mould filaments are counted by the Howard method (*Assoc. Off. Agr. Chem., Methods of Analysis*, 1935, p. 500). No field is considered positive unless the combined lengths of the two longest filaments exceeds a sixth of the diameter of the field. It is shown experimentally that mould is evenly distributed in butter and that 10-g. samples are representative of large masses of butter. An investigation of 65 commercial samples and 53 samples condemned for mould or filth showed that in 53 of the commercial samples the mould-count did not exceed 20, in 5 it lay between 20 and 40, in 5 between 40 and 60, and in the remaining 2 samples between 60 and 80, and 80 and 100, respectively. Of the 53 condemned samples, 2 gave counts between 20 and 40, 15 between 40 and 60, 20 between 60 and 80, and 16 between 80 and 100. The method employed for cream is an indirect one, the cream being first churned and the mould-count made upon the butter. Experiments were made to show that in the churning of cream the moulds concentrate in the butter. Of 144 samples collected over a period of a year, the majority (72 per cent.) gave counts not exceeding 20, and the results indicate clearly that the mould-content of butter tends to increase during the summer and autumn months.

A macroscopical method for the determination of mould in cream is carried out as follows:—Five ml. of warm cream are rinsed into a test-tube with 15 ml. of hot methylene blue and borax solution (30 g. of sodium borate and 10 methylene blue tablets, as used in the reductase test, in 1 litre of water). The mixture is shaken well and poured into a shallow tin pan approximately 7 in. in diameter. The pan is rocked until all the mould present has agglutinated into blue-stained masses. These are gathered, by means of a scalpel, into a circular disc, the diameter of which is measured and its approximate area in sq. mm. calculated. The following is a simpler modification:—Five grams of cream are placed in a beaker and treated with 15 ml. of hot methylene blue and borax solution. After shaking for 3 minutes the mixture is poured into a special perforated funnel. A circular disc, 1·5 in. in diameter, is cut from No. 26 gauge perforated brass having about 625 holes of 0·2 in diameter per sq. in. A 45° sector is removed, and the remainder of the disc is bent into a cone, the straight edges being soldered together; to this funnel is soldered a 0·5 in. collar. The mould clots are washed into the apex of the funnel with hot methylene blue and borax solution, the base of the inverted cone of mould is levelled with a scalpel and its diameter is measured. The results of the methylene blue and borax test (conveniently termed the MBB test) were compared with mould-counts made upon the butter churned from the same samples of cream. When present in sufficient numbers, yeasts and bacteria are also agglutinated by the alkaline solution and, for this reason, an occasional cream sample gave a high test by the MBB method with a low mould-count. Thus it is possible that high MBB results, whether showing mould or not, indicate other objectionable micro-organisms. Samples giving low MBB results also showed low mould-counts and, in general, with higher MBB results, high mould-counts were obtained. The results of the MBB test upon 235 cream samples were compared with the grader's remarks on the flavours of the samples. The comparison showed that "off-flavour" tends to be associated with the occurrence of mould. Of the samples graded as "off-flavour," 23 per cent. gave negative MBB results, thus emphasising the generally known fact that mould is not the only cause of "off-flavour." Of 27 samples giving high MBB results, only one had been graded as "normal sour," the remainder being "off-flavour." Thus 96 per cent. of the samples giving high MBB results had abnormal flavours. A. O. J.

Relation between the Staining Properties of Bacteria and their Reaction towards Hop Antiseptic. Part III. I. L. Shinwell. (*J. Inst. Brewing*, 1937, **43**, 191–195.)—*The Influence of Hydrogen Ion Concentration.*—It was shown in Part I (*J. Inst. Brewing*, 1937, **43**, 111; ANALYST, 1937, 323) that at a given *p*H (5·18) the concentration of antiseptic material communicated to wort by 0·5 per cent. of hops exhibited an inhibiting action only towards the Gram-positive bacteria, the action towards the Gram-negative species being negligible. It was also observed that on some acid-producing bacteria hop antiseptic had more effect at lower *p*H values. In Part III it is shown that the action of hop antiseptic towards different species of bacteria can only be stated when the *p*H is specified. For a given *p*H the effect upon different bacteria is capable of comparison, and the bacteria can be separated into a number of groups according to their growth. A table is appended showing the probable groupings in wort at *p*H 5·2 (approx.), which should serve as a rough practical guide; it is emphasised, however, that at any other *p*H, re-arrangement would almost certainly be necessary, for the combined effect of hydrogen ion concentration and hop antiseptic is irregular and differs according to the particular species, the effect of *p*H being more for some than for others at the same hop rate. It is suggested that the cell wall of the Gram-positive species may be pictured as a coarse mesh structure, and that of the Gram-negative species as a fine mesh, the former allowing the toxic humulone and lupulone molecules to pass through to the cell-contents, and the latter arresting their passage. D. R. W.

Agricultural

Determination of Crude Fibre in Oleaginous Seeds and Pressed Cakes made from them. J. Hladik. (*Z. Unters. Lebensm.*, 1937, **73**, 140–142.)—The following rapid modification of Bellucci's method (*Ann. Chim. Appl.*, 1932, **22**, 25) is recommended:—One g. of the material is heated with carbon tetrachloride in a wide test-tube, the liquid is filtered, and the residue is washed with carbon tetrachloride, dried at 100° C., and transferred to a 100-ml. conical flask. The defatted material is then heated under reflux with 3 to 4 ml. of nitric acid and 30 ml. of conc. acetic acid over a very small flame for half-an-hour, with frequent shaking. The contents of the flask are transferred to a 500-ml. beaker, which is filled with water and heated for 10 minutes. Some cold water is added (to facilitate sedimentation), the beaker is stood in cold water, and after the solids have settled the clear liquid is decanted. The beaker is again filled with water, 5 ml. of conc. sulphuric acid are added, and the mixture is heated for 10 minutes. After re-settling and decantation, the residual mass is boiled and filtered, with the aid of suction, through a sintered crucible. The residue is washed several times with hot water, then 3 times with alcohol and ether, dried at 105° C. for half-an-hour, cooled, and weighed. The crucible is then ignited and again weighed, and the difference between the two weights gives the weight of ash-free fibre. During the filtration the fibre in the crucible must be stirred up with a glass rod. The quantity of liquid to be filtered can be reduced by centrifuging the last quantity of water and fibre, shaking with water and again centrifuging, treating with alcohol and ether, and then filtering. The following results are quoted:

Material	Crude fibre, per cent.	
	Modified Bellucci method	Other methods
Pumpkin seed cake	17·6, 18·15	15·4, 18·7, 21·8, 19·0
Palm seed cake	12·75, 13·7	14·2, 15·95, 22·1, 16·65
Coconut cake	8·3, 8·5	12·9, 11·0
Rape seed	3·6, 3·2	— —
Rape cake	6·2, 6·4	— —
Coarse soya	5·3, 5·05	— 5·05
Coarse bread	1·17 —	1·02 (König)

E. M. P.

Optically Active Constituent of Derris Resin related to Toxicarol. F. Tattersfield and J. T. Martin. (*J. Soc. Chem. Ind.*, 1937, **56**, 77T.)—A yellow crystalline derivative has been obtained from the resins of *Derris malaccensis* and the "Sumatra-type" derris (F. Tattersfield and J. T. Martin, *Ann. Appl. Biol.*, 1936, **23**, 880, 899). The toxicarol fraction of the resin, which was precipitated from an ethereal solution with an aqueous solution of potassium hydroxide, yielded this product, which was crystallised from ethyl acetate. The crude product before crystallisation was toxic to *Aphis rumicus*, though less so than rotenone, but the inactive toxicarol derived from it had little or no insecticidal action. Yellow or yellowish-green crystals have recently been isolated from an ethyl acetate solution of a derris resin which was apparently of the Sumatra type. The crystals were difficult to purify, and it is not certain that they were pure after repeated crystallisations. The properties of the compounds were as follows:

	Crystals after potash treatment of resin	Crystals direct from resin.
Melting-point	99° C.	97° C.*
Percentage recovery of inactive toxicarol	84·5	83·4
Melting-point of inactive toxicarol	218° C.	219° C.†
$[\alpha]_D^{20}$ in 4 per cent. benzene solution	−69°	−67°
$[\alpha]_D^{20}$ in 2 per cent. benzene solution	−71°	−71°
Induced $[\alpha]_D^{20}$ per cent. 2 minutes after mixing	+303°	+321°
Induced $[\alpha]_D^{20}$ per cent. after 1 hour	+127°	+137°

* Mixed 95° to 97° C. † Mixed 220° C.

The inactive toxicarol was recovered by refluxing an alcoholic solution with aqueous potassium hydroxide solution and its m.p. was determined after two crystallisations from acetic acid. The induced rotation was obtained by the addition of methyl-alcoholic potash to a benzene solution of the crystals. These results indicate that the compound occurs in the resin in the form in which it has been isolated.

E. B. D.

The Two Ends of Straw. H. Nicol. (*Agric. History*, **1936, 10,** 3–13.)—The following table is compiled from the results of Pierre (*Recherches Expérimentales sur le Développement du Blé et sur la Répartition dans ses différentes Parties, des Eléments qui le constituent, à diverses Epoques de son Développement*, par J. I. Pierre, Oct., 1863. Caen-Imprimerie E. Poisson). The figures, expressed as weights of constituents in grams per kg. of dry matter of stem, show the degree of variation obtained:

	Whole stem	Lower part				Upper part			
Sample number	2	3	4	5	6	3	4	5	6
Combined nitrogen	12·54	7·21	4·29	3·02	1·73	21·18	18·86	9·09	4·52
Silica	9·53	10·06	11·81	12·91	16·63	13·76	22·37	17·17	30·03
Phosphoric acid ..	3·80	2·88	1·57	1·06	0·40	5·13	5·39	1·56	2·19
Lime	4·04	3·76	1·96	1·94	1·60	6·38	3·69	2·35	4·63
Potash	14·46	6·06	6·90	4·59	5·85	12·52	8·71	4·89	2·78

Organic

Determination of Isopropyl Alcohol by means of the Immersion Refractometer. J. Batscha and S. Reznek. (*J. Assoc. Off. Agr. Chem.*, **1937, 20,** 107–115.)—A table has been constructed correlating the amount of isopropyl alcohol by volume, present in mixtures of the alcohol and water, with the refractive index expressed as scale readings of the Zeiss Immersion Refractometer. A supplementary table of the specific gravities of the mixtures is also given. The percentage of isopropyl alcohol is given for each 0·2 division of the refractometer scale for each degree of temperature from 20° to 25° C., and the table refers to mixtures containing up to 25 per cent. of the alcohol. The isopropyl alcohol used (Eastman 98 to 99 per cent. grade) was refluxed with lime and distilled, left in contact with anhydrous copper sulphate for several days, decanted, distilled and re-distilled from sodium, the fraction boiling at 82·3 to 82·6° C. being collected. The sp.gr. (20/20° C.) of this was 0·7867. The aqueous mixtures were prepared by pipetting the alcohol into 50 ml. of freshly boiled, distilled water in 100-ml. graduated flasks, the mixture being rotated to dissipate the heat of solution before final adjustment to volume. Solutions containing 2, 5, 10, 15, 20 and 25 per cent. of alcohol were prepared. Temperatures were controlled by means of a water-bath kept to within ±0·2° C. of the required temperature, and the refractometer readings were taken for each solution at 20 and 25° C. The specific gravities of the same solutions were determined by means of a 25-ml. pycnometer at 20 and 25° C. A. O. J.

Testing of Acetic Acid. E. C. Craven and J. M. Kershaw. (*J. Soc. Chem. Ind.*, **1937, 56,** 72–74T.)—The published specifications and tests of the B.P. (1932), B.S.I. (1934, No. 576) and "Analar" (1934) for acetic acid are described and discussed. *Titration.*—*N* sodium hydroxide solution is prepared by Kolthoff's method (*Pharm. Weekblad*, 1921, **58,** 1413; Abst., ANALYST, 1921, **46,** 516), and contains 0·058 g. of quicklime per litre, which does not affect the titration injuriously. It remains free from carbonate and retains its strength for three months. The alkali is standardised either with potassium hydrogen tartrate which has been dried in the water-oven at 95–100° C., or, better, with standard acetic acid of high melting-point. The sample is weighed from a graduated pipette into a flask containing water and phenolphthalein already titrated to faint pink, such a quantity being taken that the final titration will be between 49·0 and 50·0 ml. *Melting-point.*—If the usual test-tube is used, moisture may be taken up and crystallisation start on the walls of the tube. A round, long-necked flask (50–100 ml.) is therefore used. It is three-quarters filled with the sample, and a finely-graduated thermometer is inserted through the cork, the thermometer bulb being in the centre of the flask. The apparatus is cooled in water to about 2° C. below the probable m.p., the flask is wiped, and the thermometer is quickly withdrawn, the bulb is touched with solid acetic acid (previously prepared), and the thermometer is replaced. Then, on shaking the flask, crystals rapidly form. The temperature rises to a maximum and remains constant to 0·01° C. for 10 minutes in a room at 18° C. With 99·0 per cent. acid the maximum error due to the supercooling is 0·04° C.; there is no error with 100 per cent. acid. Pure acetic acid melts at 16·60° C. (Bousfield and Lowry, *J. Chem. Soc.*, 1911, **99**, 1432); the m.p. is reduced 2·00° C. for 1 per cent. of water. The amount of other impurities is usually insufficient to affect the m.p. to any measurable extent, and the lowering of the m.p. below 16·60° C. may be safely attributed to water. *Residue on evaporation.*—This test is considered unsatisfactory, as errors in weighing due to the absorption of moisture by the platinum dish may amount to 0·001 g. *Iron.*—A rapid test may be made by mixing 20 ml. of the sample with 80 ml. of cold saturated salicylic acid solution. With 0·5 p.p.m. or more, a magenta tint (which may be compared with standards) develops in 10 minutes. If a 1 per cent. sodium salicylate solution is substituted for salicylic acid, the colour develops in 2 to 3 minutes, and the colour in Lovibond units for a 10 ml. depth is 0·45 red unit per 1·0 p.p.m. and pro rata to 4·0 p.p.m. *Chlorides.*—The B.P. limit (1065 p.p.m.) is considered too high. The A.R. test gives no opalescence at 2 p.p.m., but shows one at 3 p.p.m. *Sulphates.*—The B.P. limit (3000 p.p.m., as SO_3) is very high. The B.S.I. method requires 18 hours to detect 15 p.p.m.; but the A.R. test will detect 3 p.p.m. in five minutes after the preliminary work is completed. If no perceptible turbidity appears in 5 minutes after the addition of 1 ml. of barium chloride solution to a mixture of 5 ml. of the sample and 20 ml. of water, the sulphate-content is below 10 p.p.m. Turbidity is delayed or prevented if more than 2 drops of conc. hydrochloric acid are added to the solution. *Heavy Metals.*—A perceptible colour is given immediately on passing hydrogen sulphide through glacial acetic acid containing 1 p.p.m. of lead or copper. *Permanganate test.*—The effects of acetaldehyde or crotonic acid on the permanganate test are as follows:—Permanganate test × per cent. of aldehyde = 70 seconds. Permanganate test × per cent. of crotonic acid = 0·5 second. Formic acid is not detected by the test. The time for synthetic acid usually exceeds the periods specified. *Formic Acid.*—This is determined by the Agulhon method (*J. Soc. Chem. Ind.*, 1933, **52**, 239T). This usually shows the content of formic acid, etc., in synthetic acetic acid to be less than 0·01 per cent.; hence the mercuric method of the B.S.I. is unnecessary. In the specified methods using conc. sulphuric acid and potassium dichromate, it is advisable to make blank tests on acetic acid distilled with chromic acid.

E. B. D.

Determination of Oils and Phosphatides in Organic Raw Material. B. Rewald. (*J. Soc. Chem. Ind.*, 1937, **56**, 77T.)—Four portions of a sample of minced soya beans were each extracted successively with two solvents, as follows:—(*a*) With light petroleum followed by 96 per cent. alcohol; (*b*) with light petroleum followed by a mixture of 80 parts of alcohol and 20 parts of benzene; (*c*) with 96 per cent. alcohol followed by a mixture of 80 parts of alcohol and 20 parts of benzene; (*d*) with a mixture of 80 parts of alcohol and 20 parts of benzene followed by 96 per cent. alcohol. The time of extraction with each solvent was 36 hours for approximately 30 g. of soya beans. After distillation of the solvents the residues were dried *in vacuo*, dissolved in light petroleum and filtered. They were ignited with fusion mixture, and the phosphorus was determined as $Mg_2P_2O_7$. The results showed that light petroleum dissolves very little phosphatide and that no one solvent extracts all the organic phosphorus. The mixture of alcohol and benzene is the best solvent; in (*d*) this extracted 89·1 per cent. of the phosphatide, and the 96 per cent. alcohol extracted the remainder. The phosphatide is calculated on the lecithin formula with a phosphorus-content of 3·85 per cent. In extract (*b*) there is always present a little oil, which floats on the top. E. B. D.

Direct Determination of Elaeostearic Acid in Tung Oil. P. S. Ku. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 103–106.)—The elaeostearic acid of tung oil is separated from the other acids by means of aqueous alcohol solutions of proper strength at low temperatures. Two to 2·05 g. of oil are saponified with 20 ml. of alcoholic potassium hydroxide (5 per cent. in 90 per cent. by vol. of pure alcohol) by refluxing on the water-bath for 1 hour. The flask is then stood for a few minutes in a water-bath kept at 41 ± 1° C., and 25 ml. of dilute sulphuric acid (16 ml. of acid of sp.gr. 1·84 diluted to 300 ml.) are slowly added, and the temperature inside and outside maintained at 41° ± 1° C. for exactly 10 minutes, the flask being rotated occasionally. The flask is then removed, and after the addition of 25 ml. of water it is cooled in ice-water until the fatty acids solidify. The liquid is decanted from the solid cake on to a filter, with the aid of suction if necessary, the flask and filter-paper (about 7 cm. in diameter) are washed free from sulphate, the flask is turned upside down, the cake of acids is drained dry, and the filter-paper is pressed between sheets of absorbent paper. The acids on the filter-paper and in the flask are dried at room temperature in a vacuum desiccator under a vacuum of 10–20 mm. of mercury for exactly 30 minutes. They are then dissolved by pouring 25 ml. of warmed 76 per cent. by vol. alcohol through the filter-paper into the flask, which is then corked and immersed in a bath of ice and water, the bath being placed in a refrigeration box or electric refrigerator kept between −3° and 0° C. overnight. The temperature of the bath in the morning should be between 0° and 1° C. A Buchner funnel (5 to 6 cm. in diameter) is surrounded with ice and water, and the cream-like crystals are filtered off and sucked dry with the aid of a pump. The flask and elaeostearic acid are washed with 15 ml. of 60 per cent. by vol. alcohol previously cooled overnight in the refrigerator box, and, after being sucked dry, the crystals are dissolved in warmed re-distilled alcohol, and the top and tip of the funnel are thoroughly washed, 65 ml. of alcohol in all being used. The acid is titrated with 0·2 *N* sodium hydroxide solution, phenolphthalein being used as indicator; 1 ml. of 0·2 N sodium hydroxide solution = 0·05566 g. of elaeostearic acid. The precision of the method was found to be from 0·9 to 1·5 parts per 1000. Unnecessary exposure to air, warmth and light, of either the crude or the crystallised acid should be avoided, and room temperature should not exceed 25° C. The acid crystals finally obtained usually had m.p. 46° to 47·5° C. (pure α-elaeostearic acid, 48·0° C.) and a Wijs iodine value (after 1 hour's contact) of 175–183, showing that the crystals were mainly α-elaeostearic acid, but slightly contaminated with palmitic and stearic acids and traces of oleic acid. A determination of the constant error gave about −1·6 per cent., and this amount was added to the results obtained. This correction, however, is not very accurate, since the exact proportion of oleic, palmitic and stearic acids in tung oil has not yet been accurately determined. The following results were thus obtained with 7 commercial samples of tung oil:

Refractive index, n_D^{25}	1·5169	1·5172	1·5173	1·5165	1·5166	1·5176	1·5179
Iodine value (Wijs) ..	166·8	166·7	167·1	167·8	167·9	167·8	167·6
Acid value ..	2·9	3·2	2·6	2·9	2·4	1·3	1·4
Saponification value ..	191·3	191·8	191·5	191·3	192·0	190·8	191·7
Worstall's test ..	6′ 32″	6′ 25″	6′ 23″	6′ 52″	6′ 52″	6′ 23″	6′ 17″
Elaeostearic acid, per cent. (corr.)	76·14	76·55	76·70	75·51	75·78	77·19	77·55
	76·24	76·29	76·78	75·63	75·65	77·11	77·67
	76·16	76·80	76·95	75·33	75·80	77·13	77·43
	76·96	76·51	76·26	75·43	75·46	76·87	77·33
Mean	76·13	76·56	76·67	75·48	75·67	77·08	77·50
Average deviation from mean ..	0·08	0·14	0·21	0·10	0·12	0·10	0·12

On applying the method to vegetable oils other than tung oil it was found that less than 10 per cent. of residue insoluble in 76 per cent. alcohol was left except with rape oil (28·6), and cotton-seed oil (29·2). These residues, however, could not be dried, had no definite m.p., and gave low iodine values. The method was also applied to samples of tung oil containing 2·5 per cent. of six common adulterants, and the elaeostearic acid found was 1·70 to 1·98 per cent. lower than in the pure samples, the lowering being calculated at 1·3 to 1·58 for 2 per cent. of adulteration.

D. G. H.

Colour Reactions of Dinitrobenzenes in Alkaline Solution. R. Truhaut. (*J. Pharm. Chim.*, 1937, **129**, 216–221.)—A repetition of previous work (ANALYST, 1934, **59**, 431), in the light of subsequent work of others, has shown that it is necessary to distinguish between ortho- and meta-dinitrobenzenes, since these frequently give different colours. Aldehydes and ketones react readily with *m*-dinitrobenzene, and some of them also with the ortho compound, usually producing a different colour. For example, in the colorimetric determination of benzene by nitration it is the *o*-, not the *m*-dinitrobenzene (which is formed at the same time), that is estimated by the colour reaction with laevulose. Reducing sugars react only with the *o*-dinitrobenzene. Of the carbonyl compounds, uric acid and allantoin react only with *o*-dinitrobenzene, and a 1 per cent. alcoholic solution of this reagent may be used for their identification. The procedure for creatinine is to dissolve 0·1 g. in 1 ml. of a 15 per cent. solution of sodium hydroxide, and to add 1 ml. of an alcoholic solution of *m*-dinitrobenzene, a rose-violet colour, changing to strawberry-red and brown-red, being immediately formed. With *o*-dinitrobenzene, under the same conditions, a violet colour is produced slowly, and darkens as the solution becomes cloudy. Creatine gives no colour under these conditions. The sexual hormones react only with *m*-dinitrobenzene. The colour reactions previously described for certain amino acids (glycocoll, lysine, β-alanine, etc.) are due to *m*-dinitrobenzene. Phenyl-β-alanine, however, gives an immediate and intense violet colour with *o*-dinitrobenzene. D. G. H.

Volumetric Determination of Sulphur in Rubber by the use of Tetrahydroxyquinone as Indicator. R. T. Sheen and others. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 69–71.)—The tetrahydroxyquinone volumetric method (ANALYST, 1936, **61**, 503) has been modified to provide for the removal of interfering zinc, iron and other heavy metals which may occur in rubber. The rubber is oxidised by one of the usual methods. In a volume of solution, equivalent to a 1-g. sample of the rubber, the sulphate is precipitated by the addition of a known excess of standard barium chloride solution (1 ml. = 3 mg. of sulphur; 50 ml. allows a sufficient excess to precipitate up to 13 per cent. of sulphur in rubber). The liquid is then rendered just alkaline to phenolphthalein indicator with potassium hydroxide solution (10 per cent.) in order to precipitate hydroxides of zinc, etc. The precipitate is filtered off on a coarse filter-paper and washed with the minimum of water; the gelatinous hydroxide precipitate occludes the barium sulphate precipitate in such a manner that a fine filter is not required. The filtrate is diluted to 200 ml.; a 25-ml. portion is just acidified with hydrochloric acid (0·02 *N*); 25 ml. of alcohol (either ethyl or isopropyl) and tetrahydroxyquinone indicator are added, and the solution is titrated with standard sodium sulphate solution (1 ml. = 0·8 mg. of sulphur); the colour change at the end-point is from red to yellow to determine the excess of barium chloride present. Good agreement with the gravimetric method was found in tests on various samples of rubber. A determination can be made on a single sample in 20 to 30 minutes.
S. G. C.

Analytical Methods used for the Identification of Dyeing Faults on Wool. H. R. Hirst. (*J. Soc. Dyers and Colourists*, 1937, **53**, 45–50.)—*Defects due to natural and artificial impurities.*—Uneven distribution of soap residues due to the use of an excess of soap or to inadequate rinsing are indicated with a fair degree of accuracy by the presence of fatty acids and oil, which may be removed and determined by extraction with ether. If actual soap residues or oxidised oil is suspected, extraction with absolute alcohol is necessary, and the residue may be examined for total alkali, free fatty acids and oxidised and unoxidised fatty acids. Such defects may show themselves as permanent variations in shade, especially in blended wools. Sorbed alkali is determined by placing the weighed sample, from which the soap has been removed in alcohol, in a suspension of terephthalic acid in water; on the following day the acid is coagulated by heat and removed by filtration, an aliquot portion of the filtrate being titrated with standard sulphuric acid. Other indications of unevenness are *p*H measurements (which are made by the usual methods) and the yellow-brown stains developed when the samples are treated with dry steam at 100° C. or higher; this latter test will show the equivalent of 0·25 per cent. of sodium carbonate. *Dyeing faults.*—*p*H methods are used to indicate the presence of mineral acids, which may then be determined by treatment with a standard solution of sodium terephthalate (or preferably, of pyridine) and back-titration. Even carbon dioxide can influence the dyeing of wool, and in one instance it lowered the *p*H from 8 to 7·3; this impurity may be of importance, since 0·75 lb. of the gas may be liberated on scouring a wool (100 lbs. weight) oiled with 10 per cent. of oleic acid. *Metallic impurities.*—The normal amounts of the three principal metals which occur in clean commercial wool are: iron 0·003, copper 0·003, and lead 0·002 per cent. Quantities in excess of these may give trouble, especially when the wool is dyed, and, if distributed unevenly, may often be detected by dark spots visible in filtered ultra-violet light. "Spotting" with hydrochloric acid and potassium ferrocyanide may be used as a test for iron, and treatment with acidic hydrogen peroxide or potassium cyanide solution will remove copper. Existing methods, and in particular that of Allport and Skrimshire (ANALYST, 1932, **57**, 440), may be used for the determinations, wet methods being desirable for destruction of organic matter. Chromium is determined by wet oxidation, followed by titration with ferrous ammonium sulphate, with diphenylamine sulphonic acid as internal indicator. Copper in wool usually arises from dirty rolls or brass fittings, especially when a conditioning fluid (which acts as a solvent) is used. Iron is due to contact with the steel-wire parts used in the carding, combing and gilling processes, which depend for their efficiency on friction between the metal and fibres; lead is sometimes used to facilitate the tinning of iron. Iron, due to the use of an excessive quantity of catalyst to accelerate the bleaching action of the peroxide bath, is easily identified by means of ultra-violet light, because it occurs in spots and is associated with mineral oil. *Resist defects.*—Acids, alkalis, heat, light, sulphur dioxide and oils are the usual causes of uneven dyeing, and the appearance of the fault and the history of the sample are valuable indications of the origin of the fault. Fats which are solid at the temperature of the indigo-vat act as a resist, especially if the vat is deficient in ammonia. A useful test is to strip the sample with a light stripping-agent (*e.g.* ammonia, acid or alkaline sodium hydrosulphite solution), and to re-dye it. The rate of stripping depends on the treatment received prior to dyeing; undamaged wool remains coloured long after the damaged wool is completely stripped. Acid dyes on wool which has undergone severe treatment with alkali or stripping agents prior to the final dyeing are extremely fugitive to soap. *Carbonising defects.*—On stripping and re-dyeing, stains due to excessive action of acid appear lighter in shade. If, however, the wool has been damaged by alkali prior to carbonising, darker shades are produced; if an ammonia stripping-bath is used, the effect of the alkali is counteracted, although that due to the carbonising remains. *Defects due to micro-organisms.*—Pauly's reagent (*cf.* Rimington, *J. Text. Inst.*, 1930, **21**, 237T) is frequently useful to distinguish between damage on dyed and finished wool due to micro-organisms and that due to chemical or mechanical influences, as it gives a positive reaction in the two latter instances; with undyed wool it is preferable to test for micro-organisms by the usual biological methods. If a sample has been exposed to light, the *p*H value falls, and the Pauly reaction is more intense and increases with time, so that, in the absence of sulphur dioxide, these indications are evidence of damage due to light. A buffered solution of trypsin is of value both to indicate rapidly the resistance of the fibre to bacterial damage and to estimate existing damage, the time required to break down the fibre by the enzyme being proportional to the amount of damage it has undergone (*cf.* Burgess, *id.*, 1934, **25**, 289T). *Oil impurities.*—Ultra-violet light is of special value here, and may be used both to identify the oil and to indicate if oxidation has occurred. If possible, the oil should be extracted and the fatty acids liberated in the usual way, unoxidised fatty acids being separated with petroleum spirit, and oxidised fatty acids with ether; large quantities of the latter indicate a long storage period or, if the storage period has been short, an easily-oxidisable oil. *Miscellaneous defects.*—If the sample is worked for 1 hour in a cold acidic solution of Kiton Red-G, and the partly-exhausted liquor matched against a standard solution of the dye, then the amount of dye absorbed by the wool, which is a quantitative measure of damage due to chlorination, may be obtained. Methylene blue, buffered to *p*H 7, also gives good results, and may be determined by titration with titanous chloride solution. Pauly's reagent also reveals damage due to the action of light and weather on the tips of locks in the fleece. Wool damaged in this way has a greater affinity for dyestuffs, and in ultra-violet light it appears white against the blue fluorescence of the sound wool. Bands across the length of the lock, which sometimes become visible in ultra-violet light, are probably due to a seasonal change. Scorching by ironing is revealed by examination of the sample under the microscope after staining with Pauly's reagent, when the fibres affected appear swollen or burst and are deeply stained. The characteristic odour of burnt wool is detectable if the sample is placed in distilled water in a stoppered bottle overnight; other odours may also be concentrated in this way. Fibre-ends of sound wool are clean-cut (the cut being at an acute angle to the length of the fibre if a cutting-machine has been used), attack by acids or micro-organisms produces brush-shaped effects, and moth larvae cause characteristic irregularities. The Allwörden reaction (liberation of bubbles on immersion of the fibre in water half-saturated with chlorine) is satisfactory for the detection of incipient damage to wool fibres, but it does not respond to damage by alkali. A solution of Nile Blue is an aid to microscopical examination, and stains mould hyphae, fats and oils. Yellow-brown stains, which develop on stoving, have been traced to selenium in certain brands of sulphur. The wool (5 g.) should be moistened with 100-vol. hydrogen peroxide containing a few drops of conc. nitric acid and gently charred, the residue being distilled with 25 ml. of a 10 per cent. solution of bromine in conc. hydrobromic acid until the vapours are colourless. If the distillate is decolorised with sulphur dioxide and heated for 1 hour with 1 ml. of 10 per cent. of gum arabic and 5 ml. of 5 per cent. hydroxylamine hydrochloride solution, the colour may be matched on the following day against that of a standard solution of selenious acid which has been treated similarly. J. G.

Inorganic

Separation of Lead from Copper. K. M. Sil, G. C. Roy and P. N. Das-Gupta. (*J. Indian Chem. Soc.*, 1936, **13**, 747–750.)—The nitrate solution is treated with a slight excess of 3 per cent. hydrogen peroxide and strong ammonia, and the beaker is left on a steam-bath for 20 minutes. The crystalline precipitate is washed by decantation with hot water containing ammonia, returned to the beaker, dissolved by heating with a little nitric acid and hydrogen peroxide, and re-precipitated as before in dilute solution containing not more than 0·25 ml. of nitric acid per 100 ml. The precipitate is collected in a porous crucible and washed with dilute ammonia, then with absolute alcohol, dried at 110° to 120° C. for half-an-hour, and weighed as $Pb_5O_7.3H_2O$. The filtrate is acidified with nitric acid, evaporated, and boiled to decompose hydrogen peroxide, after which the copper can be determined by the usual methods. W. R. S.

Rapid Determination of Copper in Pyrites. I. Ubaldini. (*Chim. e Ind.*, 1937, **19**, 65–66.)—Copper in pyrites and calcined pyrites can be determined rapidly and accurately by direct precipitation with salicylaldoxime. One g. of the finely ground pyrites is treated with a mixture of nitric and hydrochloric acids, the resulting liquid is evaporated to dryness on the water-bath, and the residue is taken up with conc. hydrochloric acid. After dilution with hot water the solution is filtered and the residue is washed with hot water until the washings are free from iron. The filtrate is treated with 5 g. of tartaric acid and sufficient ammonia to make the reaction just alkaline, after which dilute acetic acid is added until the liquid is just acid. Copper is precipitated from this solution by the addition, in the cold, of Ephraim's reagent (*Ber.*, 1930, **63**, 1928; 1931, **64**, 1210), which is prepared by dissolving 1 g. of salicylaldoxime in 5 ml. of 95 per cent. alcohol and making up to 100 ml. with water at 80° C. Five to 6 ml. of the reagent are required for each 0·01 g. of copper in the pyrites; in general, about 15 ml. of the reagent are sufficient. The precipitate forms at once and, after brief standing, the liquid can be filtered. The precipitate is collected in a Gooch or glass crucible, washed with cold water, and dried at 105° C. to constant weight. The weight of the precipitate, multiplied by the factor 0·1895, gives the weight of copper. The results thus obtained with samples of pyrites and calcined pyrites of different origins agree closely with those given by the modified Duisburg method (*Chem.-Ztg.*, 1919, **43**, 729). E. M. P.

Colorimetric Determination of Iron by Means of o-Phenanthroline. L. G. Saywell and B. B. Cunningham. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 67–69.)—*o*-Phenanthroline gives an intense red colour with ferrous iron which may be used for quantitative purposes with test-solutions containing 20 p.p.m. down to 0·1 p.p.m. of iron. The following method is proposed for fruit-juice or wine and involves preliminary wet destruction of organic matter. A 2-ml. sample contained in a test-tube is heated over a free flame with 1 ml. of conc. sulphuric acid and 0·7 to 1 ml. of 60 to 70 per cent. perchloric acid. If a clear, colourless liquid is not obtained in 2 to 10 minutes, a further 0·5 to 1 ml. of perchloric acid should be added and the heating continued. One ml. of water is added, and to the hot solution is added 1 ml. of 10 per cent. hydroxylamine hydrochloride to reduce the iron to the ferrous condition; 0·5 ml. of *o*-phenanthroline solution (1·5 per cent. in ethyl alcohol) is then added, followed by concentrated ammonia in amount sufficient to render distinctly pink a piece of Congo red indicator-paper placed in the liquid. The solution is diluted to 10 ml. and the red colour is matched against a range of standards prepared by treating known volumes of standard ferric iron solution in a similar way. The colour is stated to be stable. Copper in concentration up to twice that of the iron, and aluminium and magnesium up to 10 times that of the iron, caused no interference. Results obtained on various materials agreed closely with those furnished by alternative methods of determination. S. G. C.

Volumetric Determination of Tellurous Acid. R. Lang and E. Faude. (*Z. anal. Chem.*, 1937, **108**, 258–266.)—The oxidation of tellurous acid by dichromate in hydrochloric acid solution is attended by evolution of chlorine which the authors regard, not as due to the reversible reaction $TeO_3 + 2HCl \rightleftharpoons TeO_2 + H_2O + Cl_2$, but as an induced oxidation of chloride by the dichromate, and hence prevented by the addition of a more susceptible acceptor such as manganous sulphate or cerous nitrate. The tellurite solution, containing up to 0·16 g. of tellurium and 20 ml. of strong hydrochloric acid, is treated with 15 ml. of strong sulphuric acid and a concentrated solution of 3 g. of manganous sulphate. After the liquid has been diluted to 100 ml. and cooled to room temperature, 25 ml. of 0·1 *N* dichromate solution are added for less than 0·064 g., and 50 ml. for 0·064 to 0·16 g., of tellurium. After 15 minutes' standing, the excess of dichromate is titrated with 0·1 *N* ferrous sulphate solution, with 2 drops of 0·01 *N* ferro-*o*-phenanthrolin solution as indicator. The end-point is marked by a colour-change from yellowish-green to brown. W. R. S.

Determination of Sodium by the Zinc Uranyl Acetate Method. Removal of Phosphorus. O. R. Overman and O. F. Garrett. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 72–73.)—Phosphate must be removed before applying the zinc uranyl acetate precipitation method, *e.g.* in the determination of sodium in milk-ash. The following method, involving the use of zinc carbonate to precipitate the phosphate, was found to be an improvement on existing methods: To the solution (10 to 15 ml.), containing 2 to 8 mg. of sodium, is added an excess of pure zinc carbonate, and the liquid is kept at room temperature for at least 6 hours. The solid material is filtered off, washed with cold water and rejected. One drop of acetic acid is added, the solution is concentrated by evaporation, and the zinc uranyl acetate precipitation is carried out as usual. A blank test with the zinc carbonate is advised. S. G. C.

Volumetric Determination of Minute Quantities of Bromide in Presence of Chloride. H. Doering. (*Z. anal. Chem.*, 1937, **108**, 255–258.)—The following method was found to be rapid and accurate for quantities of less than 1 mg. of bromine. The solution (20 ml.) is treated in a 50-ml. conical flask with 2·0 ml. of approximately *N* calcium hypochlorite solution, 4 drops of 2 *N* hydrochloric acid, and enough calcium carbonate to render the liquid permanently milky. The solution is gently boiled for 5 minutes (the bromide being oxidised to bromate), and cautiously treated, drop by drop, with 1 ml. of 20 per cent. sodium formate solution for the decomposition of the excess of hypochlorite. After another 5 minutes' boiling the flask is well cooled in running water, the solution is acidified with 2 to 3 ml. of *N* hydrochloric acid, and treated with a few crystals of potassium iodide and 1 drop of 10 per cent. ammonium molybdate solution (catalyst). The solution is titrated with 0·002 *N* thiosulphate from a micro-burette until the yellow colour becomes faint, and the titration is finished after the addition of a drop of fresh starch solution. A blank test should be made, as the hypochlorite solution contains a trace of bromine. The process may be used for larger quantities of bromine (*e.g.* 50 mg.) on a suitably increased scale. An excess of calcium carbonate should always be present, and 1 ml. of sodium formate solution used for every 5 ml. of hypochlorite solution. The catalyst can be dispensed with, but larger amounts of 2 *N* hydrochloric acid (8 ml.) and an excess of potassium iodide are used in the final titration. Chlorate, which is formed during the oxidation, does not react with iodide under the above conditions.

W. R. S.

Dioxane as a Reagent for Qualitative and Quantitative Estimation of Small Amounts of Iodine. A. Saifer and J. Hughes. (*J. Biol. Chem.*, 1937, **118**, 241–245.)—In the qualitative test 1·0 ml. of a solution containing 0·1 mg. or more of iodine (as iodide) was placed in a test-tube and rendered just alkaline to litmus by addition of nitric acid or sodium carbonate solution. Three ml. of dioxane (diethylene oxide) were added, the solution was warmed on a water-bath, and one or two drops of conc. nitric acid were then added to the solution. The immediate appearance of a golden-yellow to an orange colour showed the presence of iodides. Thiocyanates, cyanides, carbonates, sulphides, bromides, chlorides, ferrocyanides, ferricyanides, chromates, and iodates, even when present in large amounts, did not interfere with the reaction. In the quantitative test solutions containing known amounts of iodide ion, from 0·127 to 12·7 mg of iodine, were pipetted into small calibrated volumetric flasks (3 ml. and 5 ml.) and made up to volume with pure dioxane. The yellowish-orange colour which developed was matched in a micro-colorimeter. The method was applied to iodised salt by transferring 2 g. or 3 g. of the salt to a centrifuge tube, and adding 5 ml. of dioxane and 1 drop of conc. nitric acid. The tube was stoppered shaken and centrifuged. The supernatant fluid was poured off, and the colour was matched in a micro-colorimeter against a known standard. Bromides and ferricyanides in large amounts had a slight effect on the quantitative test The method is being investigated for the estimation of iodine in biological fluids

S. G. S.

Gas Analysis

Determination of Ozone at Great Dilutions, based on the Catalytic Effect Exercised by this Gas on the Oxidation of Aldehydes. E. Briner and E. Perrottet. (*Helv. Chim. Acta*, 1937, **20**, 293–298.)—Existing chemical methods are inadequate for the determination of ozone in the state of dilution in which it occurs in air (*e.g.* concentrations of 10^{-5} to 10^{-6} per cent.), since the most reliable of them respond only to 0·01 per cent. The oxidation of a solution of benzaldehyde in carbon tetrachloride or of butyric aldehyde in hexane by the catalytic effect of ozone has therefore been utilised, the calculation being based on the equations, $C_6H_5CHO + O_2 = C_6H_5CO_3H$ (perbenzoic acid), and $C_6H_5CO_3H + C_6H_5CHO = 2C_6H_5COOH$. The increase in acidity due to the benzoic acid is measured, allowance being made for the results of a blank experiment in which gas free from ozone is used. In a typical experiment the air under investigation was bubbled at the rate of 10 litres per hour through a solution of 5 g. of benzaldehyde in 20 ml. of solvent in the dark, the temperature being maintained constant. Figures are given relating the concentration of known mixtures of ozone and air (0·1 to 0·00001 per cent. of ozone), the increases in acidity, and the corresponding number of molecules of "mobilised oxygen," calculated according to the above equation. If the log. of the concentration is plotted against the increase in acidity, the graph is almost a straight line for dilutions up to 0·001 per cent., and this graph is used when operating the method with samples of unknown concentrations. If less than 10 litres of sample are available, the smaller quantity should be used at the same rate and the time noted; the increase in acidity which would have been produced in 1 hour may then be calculated, and the graphical results applied. The catalytic effect is much greater for mixtures of ozone with oxygen than with air, and its sensitiveness increases with dilution. If a solution of 5 g. of butyric aldehyde in 20 ml. of hexane is used (*cf.* E. Briner and A. Lardon, *id.*, 1936, **19**, 850) it is possible to measure quantities of the order of 10^{-6} per cent., and this corresponds with an increase in acidity of 2·5 ml. of 0·1 *N* acid. This is an average value obtained from successive experiments which gave values of 2·6 and 2·4 ml. (*cf.* E. Briner, *id.*, 1936, **19**, 283; 1937, **20**, 282). J. G.

Microchemical

Qualitative Micro-Analysis by Electrolysis and Spectrography. A. Schleicher and L. Laurs. (*Z. anal. Chem.*, 1937, **108**, 241–247.)—For the detection of the alkali and alkaline-earth metals the solution is electrolysed in a platinum cup (capacity about 0·2 ml.) with an amalgamated copper wire (500γ of mercury) as the cathode. The latter is placed along the optical axis of the spectrograph, and at the conclusion of the electrolysis the platinum cup is replaced by another copper wire, a spark being made to pass between the two wires. In order to remove the mercury vapour during sparking, the two wires are surrounded by a small horizontal glass tube connected with a vacuum pump and provided with two slits for the passage of the wires. Hydrazine hydrate is added to the electrolyte as a depolariser. The neutral solution (0·1 ml.), containing 0·1 to 100γ of metal as chloride or bromide, is electrolysed for 15 to 30 minutes with 5·5 volt and 60 milli-amp. The operation is interrupted without washing of the cathode, and the spark is passed as soon as the electrolysis is complete. The sensitiveness varied from 1 to 10γ; the detection of potassium, however, was not practicable with the apparatus employed, two of the available potassium lines coinciding with the strong mercury line 404·6*m*μ. The above-described operations complete the authors' scheme of qualitative micro-analysis. An unknown solution is electrolysed first in acid, then in ammoniacal solution, and the deposits are tested by sparking. Any precipitate formed by addition of ammonia is collected in a filter-stick and tested spectrographically. The alkalis and alkaline earths are in the ammoniacal filtrate, which is evaporated on a platinum lid, and the residue is carefully heated to remove ammonium salts. The fixed residue is dissolved and tested as described above. W. R. S.

Micro-determination of Magnesium Sulphate. M. Möller and G. Schlegel. (*Mikrochem.*, 1935, **18**, 159–161.)—Emich's involution method (*Mikrochem.*, 1933, **8**, 283; Abst., ANALYST, 1933, **58**, 784) has been tested with unweighable amounts of magnesium sulphate. The sulphate is precipitated with barium hydroxide, the precipitate consisting of barium sulphate and magnesium hydroxide. The hydroxide is converted into sulphate by means of sulphuric acid, the excess of acid is removed, and the precipitation is repeated again and again until the precipitate may be weighed with sufficient accuracy. A glass micro-beaker and Emich filter-stick with asbestos filtering medium are used for the precipitation and filtration. The micro-beaker is placed inside a glass tube, 3·3 cm. wide, closed with rubber stoppers at both ends. The stopper at the top has 5 holes fitted with narrow glass tubes: one for running the barium hydroxide solution (0·03 molar) into the beaker, the second for running in distilled water, and the third connected with the filter-stick, which can be lowered into the beaker, and attached to the filter-pump when required. The fourth and fifth tubes are so arranged that a current of an inert gas (hydrogen) may be passed through to prevent a contamination with barium carbonate. After each precipitation the precipitate is washed carefully with water free from carbon dioxide; the beaker and filter-stick are then disconnected and placed under a small bell-jar with a tube for attachment to the pump and a tube open to the atmosphere, to which the filter-stick standing in the beaker is attached. By using slight suction small portions of dilute sulphuric acid are drawn through the filter in the reverse to the usual direction, to dissolve any magnesium hydroxide adhering to the asbestos filter. The filter-stick is then washed with water, the solution and washings in the beaker are evaporated to dryness, and the excess of sulphuric acid removed by careful and prolonged heating at about 325° C. After a sufficient number of repetitions (5 or 10) the beaker and filter-stick are weighed with the precipitate. Errors varying from +2 to +8 per cent. were obtained in the determination of 0·05 to 0·1 mg. of magnesium sulphate. J. W. M.

Sensitive Reaction for Chlorates, Bromates and Sulphites. I. M. Korenman. (*Mikrochem.*, 1936, **20**, 225–226.)—Two ml. of the neutral or acid chlorate solution are treated with 0·5 ml. of saturated sodium sulphite solution, 3 to 4 drops of a 0·02 per cent. aqueous solution of indigo carmine are added, and the mixture is acidified with 1 ml. of 3 N hydrochloric acid. If the blue colour rapidly disappears the presence of chlorate is indicated. The limit of identification is 0·4γ of potassium chlorate in 2 ml., and the concentration limit is 1: 5,000,000. The reaction may be carried out as a spot-test by placing one drop (0·03 ml.) of chlorate on the spot-plate, followed by 1 to 2 drops of 0·02 per cent. indigo carmine solution, 1 drop of saturated sodium sulphite solution and 1 drop of 3 *N* hydrochloric acid. The mixture is rapidly decolorised, while a blank test remains coloured. The limit of identification is 0·2γ $KClO_3$ in 0·03 ml., and the concentration limit is 1: 160,000. The decolorisation of indigo is not specific for chlorates, as some other oxidising agents, such as bromates or chromates, behave similarly. The sensitivity of the test applied to bromates is as follows: in a test-tube the limit of identification is 0·66γ of potassium bromate in 2 ml., and the concentration limit is 1: 3,000,000; as a spot-test the limit of identification is 0·24γ in 0·03 ml., and the concentration limit is 1: 125,000. By means of this reaction as little as 0·001 per cent. of potassium bromate may be detected in potassium bromide. Oxidising agents such as permanganate and hypochlorite decolorise indigo carmine in the absence of sulphite. Other oxidising agents do not decolorise indigo carmine, but potassium ferricyanide and potassium iodate impart a green colour to the solution under the conditions of the test. When applied as a test for sulphite the reaction is carried out as follows:—Two ml. of a solution of sulphurous acid or sulphite are treated with 0·5 ml. of saturated potassium chlorate solution, and then acidified with 1 ml. of 3 *N* hydrochloric acid, and 2 to 3 drops of 0·02 per cent. indigo carmine solution are added. In the presence of sulphite the blue colour disappears. The limit of identification is 2·5γ of sulphur dioxide in 2 ml., and the concentration limit is 1: 800,000. For a spot-test, 1 drop of the test solution is mixed with a drop of a mixture of 1 volume of 0·02 per cent. indigo carmine solution, 1 volume of saturated potassium chlorate solution, and 2 volumes of 3 *N* hydrochloric or sulphuric acid. In the presence of sulphite the blue colour of the drop rapidly disappears. The limit of identification is 0·5γ of sulphur dioxide in 0·03 ml., and the concentration limit is 1: 60,000. Sodium sulphide (1 part in 30,000) and sodium thiosulphate (1 part in 15,000) also give this reaction.

J. W. M.

Methods of dealing with Small Quantities of Liquids and Precipitates. B. L. Clarke and H. W. Hermance. (*Mikrochem.*, 1935, 18, 289–302.)—*Capillary siphon pipettes.*—These are made from narrow tubing drawn out to a capillary at one end, the capillary portion being bent over and down to form a U-bend. The length of the capillary portion may vary, but, as these pipettes are most useful for removing the supernatant liquid from centrifuge tubes, the length is so adjusted that the tip will reach the bottom of the centrifuge tube, and being slightly bent over, will touch the walls of the tube. The other end of the siphon tube (the length is approximately twice that of the capillary portion) is bent round, and a wider tube ending in a bulb with an outlet-tube is attached. Slight suction or pressure may be applied to the top outlet-tube from the bulb to assist, retard or reverse the flow. For continuous work a bottom outlet, vertically below the bulb, is useful; it is closed by a short rubber tube plugged with a glass pellet, and an air bubble prevents contact between the rubber and the liquid. The siphon pipettes are convenient for the addition of wash liquids to the centrifuged precipitate and also for stirring the contents of the centrifuge tube by means of a stream of air bubbles blown through the siphon. A supporting stand, with rack-and-pinion adjustment for the height of the siphon orifice, and a spring clip for holding the centrifuge tube, are convenient. *Filter.*—The siphon pipette is modified to give a micro-filter of the Emich filter-stick type. The capillary orifice of the siphon is replaced by a small bell-shaped opening into which a pellet of filter-paper pulp is packed. The descending arm of the siphon is elongated to provide sufficient head of liquid to overcome the resistance of the filter. The filter, which may be detachable, is connected with the siphon by rubber tubing; it is especially useful when the precipitate on the filter has to be re-dissolved, as liquid passes readily through it in either direction. *Steam-jacketed capsule for evaporation.*—The apparatus is designed for the rapid evaporation of a few tenths of a ml. as in qualitative analysis. A glass bulb, about 2 cm. in diameter, is blown in the middle of a tube, and a portion of the wall is heated and sucked in to form a small basin enveloped by the remainder of the bulb. One of the tubes attached to the bulb is drawn out and bent upwards to form a nozzle of about 1 mm. bore, whilst the other is bent downwards at right angles to the axis of the bulb and inserted in the rubber stopper of a conical flask, which serves as a steam generator. A steam-jacket is thus formed, while the exhaust nozzle increases the velocity of the escaping steam and serves to blow it away from the basin while, at the same time, creating a slight current of air which aids evaporation. *Hydrogen sulphide precipitation and pressure digestion.*—The bulky, slimy precipitate is normally difficult to filter and wash satisfactorily on the micro-scale. An improvement is effected by carrying out the precipitation in closed tubes in which hydrogen sulphide may be generated at a pressure of several atmospheres by thermal hydrolysis of thioacetic acid. The precipitates formed in this way are relatively dense and granular, easily filterable, and show no tendency to go into colloidal solution on washing, and floating is eliminated. *Method.*—The solution is introduced into the tube by means of a capillary pipette or siphon. The solution should not occupy more than a fourth of the volume of the tube when sealed off. Thioacetic acid is added from a capillary pipette, about 0·005 ml. per mg. of metal expected, with a minimum of 0·01 ml. for a tube of 5 ml. capacity. The upper part of the tube is drawn out and sealed in the flame. The tube is placed in a beaker of boiling water, and the contents are stirred by spinning the tube on its axis. After precipitation is complete the precipitate is centrifuged, the tube is opened, the supernatant liquid is removed with the siphon pipette, and the precipitate is washed by centrifuging. To re-dissolve the sulphides, a few hundredths of a ml. of acid may be added, and the tube is sealed and heated. In this way less acid is needed and risk of loss by spirting or volatilisation is avoided. *Micro-distillation apparatus.*—The apparatus is designed to avoid explosive ebullition and also contamination of the distillate by foam when boiling liquids of high surface-tension—troubles largely due to the narrow bore of micro-distilling tubes. The distilling chamber is in the form of a greatly flattened bulb, which gives a very large surface without increase of volume. The sample is introduced through a stoppered tube at the side of the bulb and is absorbed in a layer of coarse (10-mesh) sand. Heating is uniform over the flat surface of the bulb (diameter about 3 cm.), which rests on an aluminium block heated either by a micro-burner or electrically. Above the distilling bulb is a small tower, the height depending on the boiling-range of the liquids. The tower has several thin-walled bulbous internal projections (made by sucking in the heated wall), which act as baffles to arrest spray, reduce volume, and produce a slight fractionation effect. The vapours are conducted from the top of the tower through a side-tube connected with the receiver, which is suitably cooled. J. W. M.

Physical Methods, Apparatus, etc.

Method of Determination of Error in Measurement of Small Particles by the Microscope. F. Ehrenhaft. (*Compt. rend.*, 1937, **204**, 40–41.)—Owing to diffraction of light, the images of very small particles observed microscopically may appear too large. Whilst the error can be minimised by photomicrography in ultra-violet light or by the use of an objective of large aperture (1·6), the following expedient has been employed for visual measurement. Two small spherical particles of the same material and of equal size are selected (the radii may be measured by ultra-violet photomicrography). The particles are observed visually under the measuring microscope and are manipulated so that they touch one another; the images may encroach owing to enlargement by diffraction. The diameter of image perpendicular to the line joining the centres, and also the length of the combined image along the line of centres, are measured. Owing to encroachment of the images, the second value will be smaller than the sum of the diameters perpendicular to the line of centres, giving a direct measure of the error involved. The work was carried out in connection with determination of the mobility of small spheres in a gas. S. G. C.

Apparatus for the Measurement of the Hydrogenation Value. A. Castille. (*Bull. Soc. Chim. Belg.*, 1937, **46**, 6–9.)—A 250-ml. reaction flask made of thick pyrex glass contains in its elongated base an agitator which is constructed of platinum-iridium and built up from three horizontal perforated discs, and a fourth bottom disc which is slightly bell-shaped, and serves to project the liquid against the walls of the flask. To the top end of the shaft of the agitator is attached a small cylinder of soft iron which is arranged between the poles of an electro-magnet in such a way that when the current supplied to the latter is interrupted every second (by means of a mercury contact operated by an electric pendulum), the agitator falls into the liquid, carrying with it, between its discs, the hydrogen necessary to effect reduction. About 0·1 g. of the sample is weighed into the small glass cup, which is then covered and suspended in a platinum ring 2 cm. above the surface of the liquid in the flask (see below); at the correct stage the magnet is raised, when the agitator also rises and the top disc strikes the cup and distributes the contents into the liquid. The pressure of the hydrogen is measured by means of a two-arm type of manometer, which is connected directly with the reaction vessel through the tube in which the agitator-shaft revolves. Any suitable catalyst may be used, but a suspension of 1 g. of spongy platinum (prepared by Loew's method) in 25 ml. of glacial acetic acid is preferred, and this volume just covers the top disc of the stationary agitator. The hydrogen should be washed and dried, and clamps are provided for making the outlet of the reaction-vessel air-tight. Before the experiment starts, suction is applied five times, so as to remove as much air as possible from the system; the air is replaced each time by hydrogen, so that eventually a pressure of 1 atmosphere of this gas is obtained. The agitator is started and, after a few minutes, the catalyst is saturated with hydrogen, and when an equilibrium-condition has been reached the temperature and pressure are noted. The sample is then added, the pressure is maintained as nearly as possible at the same value by adjustment of the levelling-tube on the manometer, and, after 15 minutes, absorption is complete. Then the hydrogenation value is given by 0·8987 × volume of hydrogen absorbed corrected to N.T.P./weight of sample; an index of 100·8 is equivalent to an iodine value of 126·9. The method has been used to examine two strongly-unsaturated compounds from Boleko oil, *viz.* an aldehyde which, on catalytic reduction, produces *n*-decane, and a C_{20} compound which, on saturation, forms an acid $C_{20}H_{40}O_2$; the sensitiveness was found to be ±0·5 and 0·1 per cent., respectively. J. G.

Restoration of Obliterated Passages and of Secret Writing. L. Bendikson. (*Franco-American Review*, 1937, **1**, (3), 1–19.)—Passages written in ink and subsequently obliterated with another ink may sometimes be deciphered by making photostat negatives and examining the enlarged prints therefrom under the microscope. The superimposed ink-strokes can then often be picked out and eliminated with a brush and Indian ink, leaving the original words in white on a black background. By this means the author deciphered several obliterated passages in the letters of John Jay and Benjamin Franklin, the American statesmen.

The invisible ink used in a number of letters written in 1776 by Silas Deane, an agent of John Jay, was shown experimentally to have been a solution of gallotannin, the writing having been developed with a solution of ferrous sulphate. Hitherto, the formula of the secret ink devised by Sir James Jay (brother of John Jay) has remained unknown.

Luminescence and its Applications. J. T. Randall. (*J. Roy. Soc. Arts*, 1937, **85**, 353–380.)—The history of luminescence phenomena is first briefly reviewed, after which, the classes of luminescent inorganic and organic materials and the preparation of inorganic phosphors are discussed; chemiluminescence, flame luminescence, thermoluminescence, bioluminescence and true phosphorescence phenomena are included, and special reference is made, with the aid of illustrations, to the spectra of luminescent materials. The effects of changes in temperature on the luminescence of a body are then dealt with, special reference being made to zinc sulphide—cadmium sulphide powders, and the connection between the optical and electrical properties of luminescent solids is illustrated by curves relating the luminescence and electrical conductivity of zinc sulphide, which also show clearly the effects produced by heating during phosphorescence. This leads to a consideration of the electronic theory of the subject, which, it is considered, provides an adequate qualitative explanation of the width of the spectral bands and also of phosphorescence and of the effects of impurities. The following applications of luminescence are discussed:—Fluorescence analysis in ultra-violet light; uses (*e.g.* for fluorescent screens) in *X*-ray work; the excitation of radiations by the use of fluorescent powders in discharge tubes—a process which has enabled the efficiency of high-voltage tubes to be raised to values which are in excess of those of tungsten filament lamps of similar voltage. Neon discharge tubes coated with calcium tungstate or zinc orthosilicate produce pink or yellow coloured light, respectively, and the efficiency is high and is maintained over a much longer period than with mercury tubes. Actually, the luminescence from both powders is the same, and it is the use, in conjunction with mercury or neon, which determines the final colour. The range of colours obtained by combinations of this kind and the corresponding luminous efficiencies are tabulated. Fluorescent sulphides of zinc and cadmium will withstand the conditions imposed by high-pressure mercury arcs, and may be used to increase the red constituent of the radiation. Cathode-ray tubes for television are also coated with mixtures of such powders. J. G.

Reviews

INORGANIC CHEMISTRY: A SURVEY OF MODERN DEVELOPMENT. SIR GILBERT T. MORGAN, D.Sc., Sc.D., LL.D., F.R.S., F.I.C., and FRANCIS HEREWARD BURSTALL, M.Sc., A.I.C. Pp. 462. Cambridge: W. Heffer & Sons Ltd. Price 15s.

One's first feeling on glancing through the contents of this curious and fascinating book is one of mild surprise coupled with a speculative wonder as to the causes that led to its being written at all; one's second, on settling down in earnest to read it, is a sincere thankfulness that it has been written, whatever the causes may have been. It seems impossible to classify it under any of the ordinary headings; it most certainly is not either a text-book or a reference book; neither is it entirely of the type of, say, "Recent Advances," though much more akin to that, for large sections which might come suitably under the title "Inorganic Chemistry," are omitted entirely; it is not by any means a "Popular Science" manual, for its condensation, though masterly, is severe, and in many parts it needs a good deal of knowledge of the subject to follow it intelligently. A résumé of the contents is, perhaps, the best method of indicating the unusual character of the book. An introduction of 36 pages deals chiefly with radio-activity, the constitution of the atom, the classification of the elements and valency; after this comes a systematic though somewhat unorthodox account (217 pp., *i.e.* about half the book) of all the elements arranged under their periodic groups. These are followed by "Transmutation of the Elements," "Co-ordination Compounds in Nature and in the Arts," "Corrosion of Metals," "Intermetallic Compounds," "The Carbides," "Metallic Carbonyls," "Nitrosyl Compounds," and "Organic Derivatives of Metals and Metalloids." In the account of the elements the balance is entirely different from that of an ordinary text-book; for instance, hydrogen receives 3 pages and deuterium 14; bismuth hydride has a quarter of the entire space given to bismuth compounds, and the amminated trihalides of bismuth another quarter; rhenium occupies twice the space of manganese.

The "Leitmotif" of the account of the elements is the co-ordination theory; in the later chapters this drops to a great extent into the background; one has the feeling that the section dealing with the elements has largely for purpose the illustration of the theory rather than *vice-versa*. Limitations of space have led to the adoption of a system of references which has much to recommend it in a book of this kind; instead of the full reference only the author and the year are given, a considerable economy of space being thus effected.

The book is very clearly written, in spite of the double handicap of great condensation and difficult subject-matter; only very occasionally does one find a phrase which seems misleading, as, for instance, the suggestion (p. 4) that argon, cobalt and tellurium do not conform to Moseley's atomic number rule, or (p. 3) that the "fourth state of matter" is "*characterised by the emission* of cathode rays." It is pleasant to see the compound $H_2S_2O_4$ referred to as "hydrosulphurous acid" (p. 161), in spite of the earnest endeavours of systematists to make confusion worse confounded. The printing and presentation of the book are admirable, and misprints are very few, though not entirely absent.

Those of us who began our chemical careers somewhere round about 1897 have been contemporary with many startling discoveries and transformations in our science; we read about them (hastily as a rule) in the current scientific journals, and made resolutions to go more deeply into them when time permitted: then probably forgot all about them. This book gives us the opportunity of keeping at least some of these half-forgotten resolutions, of retracing some of the perplexing currents of the past 40 years and of speculating whither those currents seem now to be trending.

B. S. EVANS

BELL'S SALE OF FOOD AND DRUGS ACT. By R. A. ROBINSON. Ninth Edition. Pp. xxviii + 321. London: Butterworth & Co., Ltd. 1937. Price 15s.

When a book attains a ninth edition, general criticism is disarmed. The book has obviously met a need and filled it well. Comparison with the eighth edition shows an increase of twenty-two pages. The most important addition is fourteen pages of Merchandise Marks (Imported Goods) Orders, 1930–5. They relate to fresh and dried fruits, honey, fish, malt products, etc. The Merchandise Marks Act, 1926, is given in full, but not the principal Act of 1887. Two new appeal cases under the Act are reported.

Not much use is made of this Act in adulteration cases, but at times it might be worth considering as to whether action might not be taken under it. If an adulterated article, innocently sold by a retailer, bears a false label, action could be taken directly against the packer, who may not be the wholesaler, without any question of the wording of the invoice.

As the principal Act gives a Food and Drugs authority no permission to incur expense, it is possible that if costs were given in an abortive prosecution, the members of the Committee authorising the prosecution might be personally liable for them. A very successful Birmingham prosecution was taken for packing margarine in Danish butter boxes bearing the "Lur" brand, but the Danish Government undertook responsibility for any costs.

The Sale of Food (Weights and Measures) Act, 1926, is given in full, with an account of thirteen appeal cases heard during the last six years. Occasionally an adulteration case may be the forerunner of one under this Act. A Birmingham roundsman, after being fined for well-watered milk, was found to be selling a genuine article, but, to compensate for the missing water, he gave very short measure.

The longest section of the book, and the most important one for Public Analysts and Sampling Officers, is that dealing with the Food and Drugs (Adulteration) Act, 1928. It occupies 98 pages, and has very full notes and abstracts of appeal cases. Apparently there have been very few since the last edition (1931). Three are given, but no reference has been found to the following five cases:—*Wellings* v. *Weavers* (1933). The officer paid, unnecessarily, for a sample of milk taken in course of delivery, but that payment did not invalidate the prosecution. *Greenwood* v. *Hannam* (ANALYST, 1933, **58**, 402) decided that it was not necessary to bulk three churns of milk before sampling. *James* v. *Clarke* (1935). Division of a sample of milk was satisfactory, though the vendor, who might have done so, did not actually see it. *Atterton* v. *Wilcocks Stores* (1933). The word "butter," unqualified, did not make the invoice a warranty of genuineness. *Pottier* v. *Woolworth & Co.* (ANALYST, 1936, **61**, 31) was on the sufficiency of an initialled invoice.

It is worth noting that page 182, in the eighth edition, which suggested forms of certificates for three articles, has been entirely left out and nothing given in its place. The review of that edition in THE ANALYST criticised one of them. Apparently the author of the book is now afraid to commit himself. This is rather a pity, as a few certificates which had been found satisfactory in the law courts would be suggestive and useful in compiling a document which has so many pitfalls.

One thinks that three older appeals on the form of the certificate are worth noting. *Smith* v. *Jeffreys* (1897), where the use of "*added* water" in a whisky certificate, instead of "*excess* water," led to a case being dismissed, as the deficiency was due to evaporation. *Allwood* v. *Gregory* (1905). "Margarine, containing only 3 per cent. of butter," was accepted. *Cook* v. *Johnson* (1918) decided that a certificate may quote recommendations of the Local Government Board. With regard to evidence, *Davis* v. *Blackman* (ANALYST, 1925, **50**, 20) is important. Magistrates must not refuse to hear evidence as to the composition of other milk samples taken in the district. Minima were suggested as being of more value than averages. During the war, evidence as to other samples of camphorated oil would have been useful, but a former Birmingham Recorder refused that evidence. *Bell* v. *Mallison* (1904) ruled that the use of the word "pure" was unnecessary when purchasing for analysis.

The Milk (Special Designations) Order of 1936 has taken the place of that of 1923, and circulars relating to it account for about seven extra pages. The notice by the Commissioners of Customs and Excise in relation to misdescription of articles as spirits or beer is given. In addition to the usual references to law reports, the English and Empire Digest and Halsbury's Statutes are now regularly cited as well. Another useful innovation is the addition, to the headings of pages, of the number of the sections of the Act given below.

The Appendix on "Chemical Notes" (13 pages), which, at the head of subsequent pages, is more appropriately described as "Notes on Adulteration," has been revised but hardly brought up to date. There are new sections on chocolate roll, cream buns and pastries, ice-cream, fish (substitution of cheaper fish), and fatty oils (reference to the work of the British Standards Institution). There are, however, no references to recent actions for dried mint (Ailanthus leaves), cinnamon (sandy matter), cheese sandwiches (margarine cheese) and sultanas (sulphur dioxide). Under "Milk," there is an unfortunate statement that "a watered sample gives a freezing-point *lower* than —0·53°." It should be "*higher*," *i.e.* nearer 0°. It is curious that the heading "Colouring Matters in Food" occurs twice (pp. 312, 319). Under "Drugs," observations are made as to the authority of the British Pharmacopoeia as a standard, but there are no remarks about individual drugs such as mercurial ointment.

Under the heading "Port Wine," reference might have been usefully made to the two appeal cases, *Holmes* v. *Pipers* (1913) and *Sandeman* v. *Gold* (1924), relating to "British Tarragona Wine" and "Tarragona Port," respectively.

Under "Sago," it is stated that in some circumstances pearl seed tapioca may be legitimately sold as "sago." One cannot agree with this opinion. Evidence has been given in a prosecution that sago was more easily cooked than tapioca. If one is substituted for the other, a declaration should be made by a label. The appeal case, *Sandys* v. *Rhodes* (1903), only settled a point of *law*, not one of *fact*, as an appeal to Quarter Sessions would have done.

The opinion that starch in potted meats, *if excessive*, may be considered adulteration, is misleading. While meat *pastes* may perhaps contain starchy "filler," *potted* meat, salmon, etc., should be free from it, and also should not contain excess of water.

"Vinegar." The addition of sulphuric acid and the sale of diluted vinegar are described as "questionable operations." The former addition has not, I believe, been detected for thirty years or more, and numerous convictions have shown that the sale of weak vinegar is not now "questionable." Dr. Hamill's report is quoted, and also the letter of the Local Government Board on the composition of vinegar. These might have been usefully supplemented by the suggested definitions agreed by the Society of Public Analysts and the Malt Vinegar Brewers' Association (ANALYST, 1935, 65, 2).

Several omissions from the index have been noted: lysol soap, milk freezing-point, salmon and anchovy paste, etc. The Artificial Cream Act is not named under "Cream." At times, parallel references in the index do not agree. For example, under "Churns" there are references to eight pages where milk churns are mentioned, but under "Milk, churns" there is only one. There are a few errors in cross references in the text, such may easily occur when a book has been reset.

The foregoing criticisms are on matters of detail, which may easily be put right in the next edition, but generally one has nothing but praise for this useful and comprehensive book. J. F. LIVERSEEGE

INKS: THEIR COMPOSITION AND MANUFACTURE. By C. AINSWORTH MITCHELL, D.Sc., F.I.C. Fourth Edition. Pp. xi + 408. London: Charles Griffin & Co., Ltd. 1937. Price 12s. 6d. net.

This, the fourth edition of the standard and, indeed, so far as the reviewer's knowledge goes, the only text-book on the subject in the language, bridges a gap of 13 years. The author, pre-eminent in his particular sphere, needs little more introduction to the world of technical industry than he does in his official capacity to readers of THE ANALYST, while his reputation in forensic science in all that appertains to handwriting is international.

The chemistry of ink, difficult as it is and at times not a little obscure, has not developed markedly in the interval since 1924; but what progress has been made is covered by Dr. Mitchell in this edition in a very thorough manner. He has found it necessary to enlarge his work to the extent of some 20 per cent. and, in addition, to rewrite a large portion. The arrangement of the book follows the lines of previous editions. After a comprehensive historical introduction, the work is divided into three sections dealing with writing inks, printing inks, and inks for miscellaneous purposes, respectively. Under Section 1 are considered the chemical nature and treatment of the various raw materials used for writing inks from lamp black to galls, the composition of finished iron-gall, logwood, vanadium, aniline black, and coloured inks, as well as a comprehensive scheme for the technical examination of inks, handwriting specimens and the identification of forgeries. Section 2 deals with the manufacture and examination of printing inks, and Section 3 with the miscellaneous materials entering into the composition of copying, marking, safety, sympathetic, typewriter inks and so on.

Amongst new matter may be noted references to the use of lignone sulphonates in connection with writing ink, a scheme for the identification of individual constituents in inks in the form of writing, and the application of filtered ultra-violet light and of infra-red photography in the elucidation of those problems to which such methods are suited. The British Government Standard Specifications for Writing Inks, revised in 1928, are included for the first time. The available evidence upon the constitution of gallotannin is brought up to date and ably reviewed, and there is a comprehensive list of British patents.

It is as difficult to withhold admiration of the encyclopaedic scope of the matter and references in this book as it is of the erudition and industry displayed in its compilation. Practically nothing that comes to mind has escaped attention, and it is with rather impish glee that the reviewer, after careful search, asserts that he finds no specific reference to the type of *alkaline* (ammoniacal) gallotannate-iron ink, said to find favour in the United States, although the di-ammonium hydroxyferrigallate compound of Silbermann and Ozorovitz receives notice. Nor is there mention of that class of quick-drying writing fluids which depend for their efficiency upon partial destruction of the paper sizing by caustic alkali or sodium silicate.

There is no evidence that lignone sulphonate inks have proved serious competitors to iron-gall writing inks (pp. 15 and 175). Apart from the unknown quantity of permanence, the principal failing of this type lies in their liability to contain traces of free sulphurous acid to which suspicion attaches in connection with fading of the blue colour. Mineral acidity in a gallotannate-iron ink (p. 180) is now quite simply estimated by an electrometric titration using the glass electrode (ANALYST, 1935, 60, 533). The assumption upon which the method is based has justified itself repeatedly against manufacturers' known inclusions, and may now be said to render the older chemical methods obsolete. The duration of the keeping qualities of a "good ink," suggested on p. 185, is within the reviewer's experience considerably under-estimated.

Some discussion of the desiderata of lithographic inks in relation to the peculiarities of the printing processes involved might perhaps have usefully been included, having regard especially to the large and increasing use of these processes in replacing ordinary letterpress and duplicating, as in the "Rotaprint." To question the value of the inclusion of some of the older recipes and patent specifications, except for the purpose of historical record, would perhaps be ungracious in the circumstances.

None of these matters of criticism, however, detracts from the value of a work for which the highest praise is deservedly forthcoming, and which should prove invaluable to the manufacturer, to the analyst, and to those whose business it is to assist the deliberations of courts of justice.

The type and production throughout are uniformly satisfactory.

H. A. BROMLEY

ELEMENTARY QUANTITATIVE ANALYSIS. By H. H. WILLARD and N. H. FURMAN. Second Edition. Pp. 436. London: Macmillan & Co., Ltd. 1936. Price 14s. net.

This book appeared originally in May, 1933, and was reprinted three times between that date and the publication of the second edition in May, 1935; the volume under review is the first reprint of the second edition. In view of these facts, there seems little for the present reviewer to do other than to indicate the improvements embodied in the work as it now stands.

These comprise the inclusion of approximately 100 additional problems, new material on sources of error and related subjects, and notes on the effect of acidity, on certain oxidation-reduction systems and on their indicators. The chapter on electrolytic precipitation has been re-arranged, and that on neutralisation has been re-written and thereby greatly improved. Finally, considerable prominence is given to the use of ceric sulphate as a volumetric oxidising agent; this is a welcome feature, partly because the convenience of this reagent is not fully realised, and partly because the authors are particularly well qualified to deal with it authoritatively.

The work covers volumetric and gravimetric analysis and electrolytic precipitation. As befits a book for beginners (of degree-course standard), the theoretical treatment is clear, and full practical details are supplied. The occurrence, side by side, of both classical and tried modern methods is a feature of the book and, possibly, an explanation of its popularity. The new types of indicators for oxidation-reduction and adsorption titrations are dealt with fully, although tartrazine (which is one of the best adsorption-indicators) is not mentioned; nor is any reference made to organic gravimetric reagents, some of which are worthy to rank beside the recent advances mentioned.

It is interesting to note, in conclusion, that the classical Arrhenius theory of electrolytic dissociation is followed, although it is pointed out in a half-page that more satisfactory conceptions of acidity and basicity now exist. The wisdom of this is not questioned by the reviewer, but he feels that it may not meet with the approval of all teachers of the subject. JULIUS GRANT

Publications Received

CANNING PRACTICE AND CONTROL. By OSMAN JONES and T. W. JONES. Pp. xii + 254. London: Chapman & Hall, Ltd. 1937. Price 25s. net.

SOIL CONDITIONS AND PLANT GROWTH. Seventh Edition. By SIR E. JOHN RUSSELL. Pp. viii + 655. London: Longmans, Green & Co. 1937. Price 21s. net.

THE BIOCHEMISTRY OF THE LIPIDS. By H. B. BULL. Pp. ix + 169. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1937. Price 13s. 6d. net.

CHEMISTRY OF NATURAL PRODUCTS RELATED TO PHENANTHRENE. Second Edition. By L. F. FIESER. Pp. xiv + 456. New York: Reinhold Publishing Corp.; London: Chapman & Hall, Ltd. 1937. Price 35s.

THE COSMETIC FORMULARY. Edited by H. BENNETT. Pp. xix + 279. London: E. F. and N. Spon, Ltd. 1937. Price 18s. net.

AN INTRODUCTION TO FLUID MECHANICS. By A. H. JAMESON. Pp. x + 239. London: Longmans, Green & Co. 1937. Price 7s. 6d. net.

ORGANIC SYNTHESES. Vol. XVII. Editor-in-Chief, L. F. FIESER. Pp. v +112. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1937. Price 8s. 6d. net.

GOVERNMENT PUBLICATIONS. CONSOLIDATED LIST FOR 1936. H.M. Stationery Office. Price 1s. net.

BRITISH STANDARDS INSTITUTION. HANDBOOK OF INFORMATION, including Indexed Lists of British Standard Specifications and Methods of Test. 1937. Publications Dept., 28, Victoria Street, London, S.W.1.

B.D.H. CHLOROTEX OUTFIT. For Determination of Free Chlorine in Drinking Water and Swimming Pools. The British Drug Houses, Ltd., London, N.1.

INSTITUTO ARGENTINO RACIONALIZACIÓN DE MATERIALES. INFORMACIONES. (Includes provisional standards and specified methods of analysis for zinc oxide for paints.) Buenos Aires. 1937.

METODER FÖR UNDERSÖKNING AV FODERMEDELS MINERALBESTÅNDSDELAR. By T. WIJKSTRÖM. With an English Summary (Determination of Mineral Constituents in Feeding Stuffs). Stockholm: O. L. Svanbäcks Boktryckeri.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 5th, the President, Dr. G. Roche Lynch, in the chair.

Certificates were read in favour of John Short Dunn, B.Sc., A.I.C., and Ernest Turner, B.Sc., F.I.C.

The following were elected members of the Society:—Robert Alwyn Bottomley, B.Sc., A.A.C.I., Paul Haas, D.Sc., Ph.D., David Alexander Lambie, B.Sc., A.I.C., Harry Morris Rainey, and George Robertson Howat, B.Sc., Ph.D.

The following papers were read and discussed:—"The Determination of Bismuth as Phosphate," by W. R. Schoeller, Ph.D., F.I.C., and D. A. Lambie, B.Sc., A.I.C.; "The Distillation of Strong Acids," by H. I. Coombs, Ph.D., M.D.; "Resins and Pitches from Ancient Egyptian Tombs," by J. G. A. Griffiths, B.A., Ph.D., A.I.C.; and "A New Apparatus for the more Rapid and Economical Determination of the Freezing-point of Milk," by P. L. Temple.

SCOTTISH SECTION

An Ordinary Meeting of the Section was held in the North British Station Hotel, Edinburgh, on April 16th, 1937. Dr. J. F. Tocher presided.

The following papers were read and discussed:—"Trichlorethylene Vapour in Air: A Method of Determination," by Andrew Dargie, B.Sc., A.I.C.; "The Use of Selenium in the Determination of Nitrogen in Potato Tubers," by A. M. Smith, Ph.D., D.Sc., and W. Y. Paterson; "Some Reactions of Sodium Metasilicate," by R. T. Thomson, F.I.C.; and "A Note on the Composition of Boiler Water," by J. B. McKean, F.I.C.

The Properties of Calciferol

BY F. W. ANDERSON, B.SC., A.I.C., A. L. BACHARACH, M.A., F.I.C.,
AND E. LESTER SMITH, D.SC., F.I.C.

(*Read at the Meeting, April* 7, 1937)

THE NATURE OF CALCIFEROL.—In 1933 two of us, with S. G. Stevenson, reported the result of our observations on certain physico-chemical constants of ergosterol and calciferol.[1] Since that time, a very large amount of both substances has passed through our hands, and we are in a position now to define more closely the properties of the latter compound. "Pure" ergosterol, as manufactured on the large scale, is always slightly contaminated with dihydroergosterol, and this makes it difficult to define more closely the constants of the product that is now an article of commerce. On the other hand, crystalline calciferol is available as one of the forms of antirachitic vitamin, and its purity is closely bound up with its biological activity.

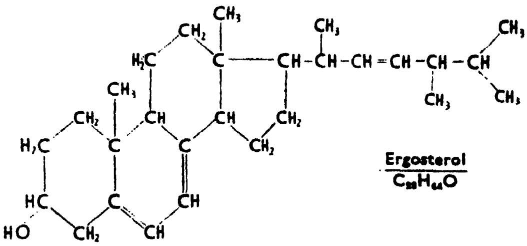

Fig. 1*a*

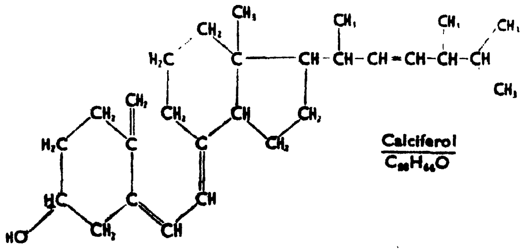

Fig. 1*b*

Moreover, calciferol is potentially the substance in terms of which the International Unit of vitamin *D* will be fixed, for the Second International Conference on Vitamin Standardisation[2] recommended in 1934 that "when the present International Standard Solution is exhausted, or if it should become unsatisfactory for any reason, . . . it should be replaced by an equivalent solution of pure crystalline vitamin *D* . . . ." The "Properties of Crystalline Vitamin *D* (Calciferol or Vitamin D_2), $C_{28}H_{43}OH$" are given in a note at the end of the Report of the Conference, and define the vitamin in terms of melting-point, specific rotation and specific absorption at 265$m\mu$. It therefore becomes important to define its properties with the greatest accuracy obtainable.

In our earlier communication we suggested provisional specifications for both ergosterol and calciferol; since then descriptions of calciferol have appeared both in the Report of the Second International Conference[2] and in the 1936 Addendum[3] to the British Pharmacopoeia, 1932. The figures given in these two descriptions are not in agreement, and it is possible that the former will be revised in the near future. It is hoped that the information to be given here may assist any revision.

In the previous paper we gave a provisional formula for ergosterol, with the reservation that the position of the two double bonds in the ring system was an open question. Since that time it has been generally accepted that these double bonds occur in the positions shown in the formula for ergosterol (Fig. 1*a*). Further, during the last two years, thanks largely to the independent work of Heilbron and of Windaus, with their colleagues, a constitution for calciferol has been put forward and has met with general acceptance. This is shown in Fig. 1*b*. According to strict definitions, calciferol is therefore not a sterol, but it is probably legitimate to include it under the general name of steroids, recently proposed by Callow and Young.[4] Another crystalline antirachitic vitamin[5] has recently been prepared, and this almost certainly contains the same steroid nucleus as calciferol, but with the side chain of cholesterol replacing that of ergosterol. According to Schenck,[5] this substance, provisionally called vitamin D_3, has the following properties:

Melting-point	82° to 84° C.
$[\alpha]_D^{20}$ (acetone)	$+83{\cdot}3°$.
$E^{1\%}_{1\,\mathrm{cm.}}$ $265m\mu$	520
Biological activity	40 international units per microgram.

Vitamin D_3 has, therefore, weight for weight, the same antirachitic activity as calciferol, when the comparison is carried out on rats.

COLOUR.—In the earlier communication we discussed the properties of calciferol under heads of source, constitution, appearance, stability, melting-point, optical activity, ultra-violet absorption at $265m\mu$, colour and other reactions and biological activity. On the appearance of calciferol—in effect, on its absorption in the visible spectrum—we have little to add to our previous observations, except that its colour in large batches may be a very pale cream, rather than white; this also depends to some extent on the size and shape of the crystals constituting the batch.

MELTING-POINT.—In our provisional specification we gave the melting-point of calciferol as 115° to 117° C. Calciferol obviously undergoes decomposition at its melting-point, which is not sharp; the Pharmacopoeial Addendum recommends that the determination be made "in an evacuated sealed capillary tube"; as, however, the range of 115° to 119° C. is given, it does not appear that this procedure has any particular advantage, since without it we find that calciferol melts over a range of at most 2° C. The mean of the upper and lower temperatures of melting for any one sample has never, in our experience, been below 115° C., and we think the description of the melting-point could conveniently be "unsharp, 116° C." In any event, amounts of impurity likely to depress the melting-point below, say, 114° C., are almost certain to be detected during determination of the other constants.

ULTRA-VIOLET ABSORPTION.—The ultra-violet absorption of calciferol is of value in checking its purity, though certain reservations must be made about the use of this constant. In the first place, likely contaminants, such as the other irradiation products of ergosterol and of calciferol itself, also have specific absorptions in the same region of the ultra-violet spectrum, and of similar intensities. Further, the error of this determination is generally accepted as being about ± 2½ per cent.; for a true value of $E^{1\%}_{1\text{cm.}} 265 m\mu = 480$ this would give a range of 468 to 492. It will be seen below how many of the determinations on actual samples fall within such a range. When, however, the value for specific absorption is taken in conjunction not only with the rather indeterminate melting-point, but also with the optical rotation, which can be measured with considerable accuracy, we consider that it is of unquestionable value as a criterion of purity. For reasons that will appear below, we propose to consider the actual absorption figures in conjunction with those for optical rotation.

OPTICAL ROTATION.—We have devoted considerable attention to the value for the optical rotation of calciferol. Serial samples both of the free steroid (in absolute alcohol) and of its 3:5-dinitrobenzoate (in pure benzene), from which it is prepared by hydrolysis, give values for optical rotation that depart by appreciable amounts from the average figure.

In Fig. 2 we show, by means of a scattergraph, the range of these values found for batches prepared from 1932 onwards. We have also indicated thereon the limits put forward in our earlier publication, in the Report of the Vitamin Conference and in the 1936 Pharmacopoeial Addendum.[1,2,3] Similar limits are indicated in Figs. 6 and 7 below. It will be observed that, not only has the spread of these values diminished year by year, but also the average figure seems to have increased from 1933 to 1935. This increase is undoubtedly associated with modifications made in the method of carrying out the observations, for reasons that will now be discussed. As a result of these modifications, moreover, only a single sample examined in 1934, and not one examined in 1935 or 1936, falls within the limits suggested for optical rotation in the Second International Conference Report.

For some time we inclined to the view that the lower values were the more correct, and that the higher figures indicated the presence in calciferol, and in the dinitrobenzoate, of some substance with a high optical rotation. That this was not lumisterol—a product occurring as an intermediate between ergosterol and calciferol during irradiation—was established by applying the procedure of Setz.[6] This consists in isomerising the substance in a chloroform solution with hydrochloric acid gas, and then heating the product for a considerable time with sodium amyloxide and amyl alcohol. Any lumisterol present is thereby partly converted into epi-isolumisterol, which, unlike lumisterol and calciferol, is precipitable with digitonin. From certain batches of calciferol with an apparently high rotation, no trace of precipitate was obtained with digitonin after the treatment described. Moreover, when lumisterol was added to a sample of calciferol in sufficient amount to raise the rotation appreciably above that of the suspected sample, the test of Setz gave a clear positive result.

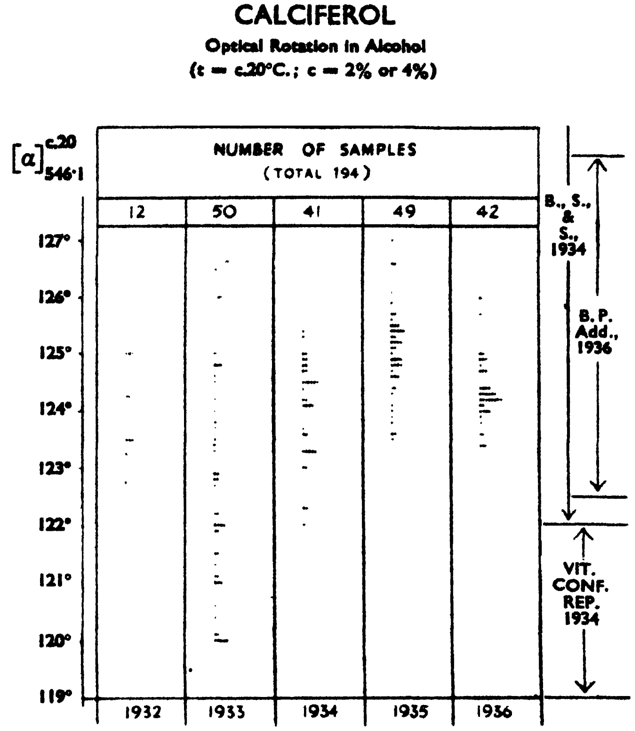

Fig. 2

We are, therefore, quite satisfied that the apparently high rotation of some batches is not to be ascribed to the presence of lumisterol, at any rate in significant quantities. Simultaneously with many unsuccessful attempts to separate some other substance having a higher rotation than calciferol, both by fractional crystallisation and by chromatographic methods from ester and alcohol, we turned our attention to the effects of concentration and temperature on the rotation. It was then found that calciferol dinitrobenzoate showed a marked increase in positive rotation with rise of temperature and a slight increase with increase of concentration. These increases are recorded in Table I; they are, in fact, insufficient to

TABLE I

CALCIFEROL DINITROBENZOATE

t° C.	$[\alpha]^{t}_{546\cdot1}$ ($c = 2$)	c (concn. per cent.)	$[\alpha]_{546\cdot1}$
14	68·0°	0·5	69·4°
20	69·25°	1·0	69·6°
25	69·9°	2·0	69·9°
32	70·5°	4·0	70·4°
40	71·4°		

Effect of temperature, t, and concentration, c (per cent. weight in volume) on optical rotation in pure benzene.

explain all the instances of high rotating ester encountered by us, but they are certainly in part responsible.

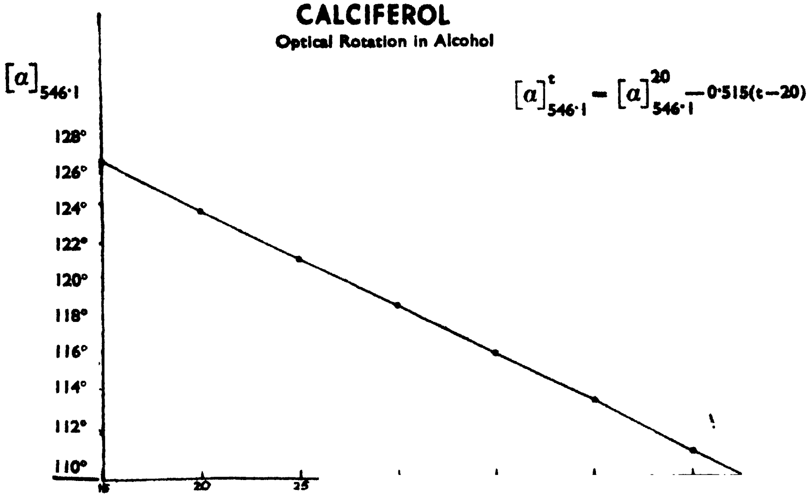

Fig. 3

The effects both of temperature and of concentration on the specific rotation of calciferol itself are even more marked; they are shown in Figs. 3 and 4. It should be noted that a rise in temperature diminishes the positive rotation of calciferol, although it increases that of the ester. The effect of increasing concentration is in the same direction for both the steroid and its ester. From 1935

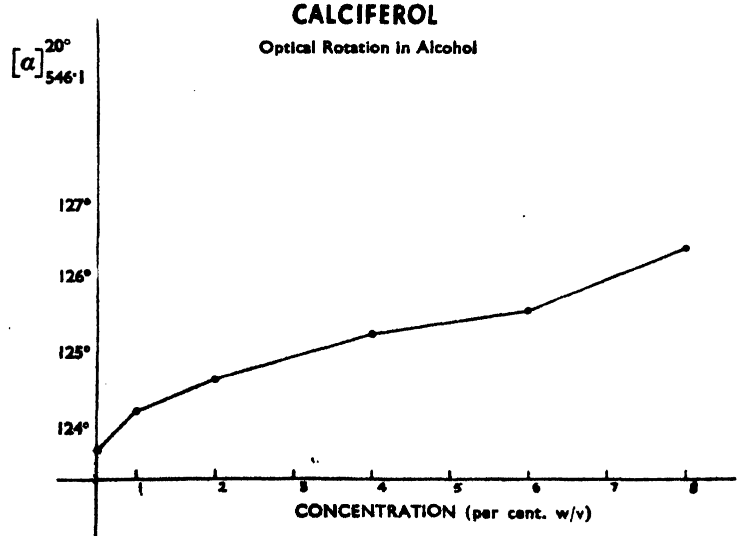

Fig. 4

onwards we have therefore made up at 20° C. ± 0·2° all calciferol solutions intended for polarimetric examination and have carefully recorded the temperature at which the optical rotation was read and, when necessary, adjusted this for the temperature coefficient obtainable from the figures plotted in Fig. 3. This coefficient indicates a change of —0·515° in the rotation for each degree rise in temperature; it can be calculated that about one quarter of this effect is due to the coefficient of thermal expansion of the solvent alcohol. We also standardised at 4 per cent. weight-in-volume the concentration of the solution that we examine. These changes are expressed in the smaller range of rotations and the higher average rotation found in samples for 1935 and 1936, to which reference has already been made.

There is little effect of concentration on the specific rotation of ergosterol, but changes in temperature operate as on calciferol, and to about the same extent. This effect is shown in Fig 5.

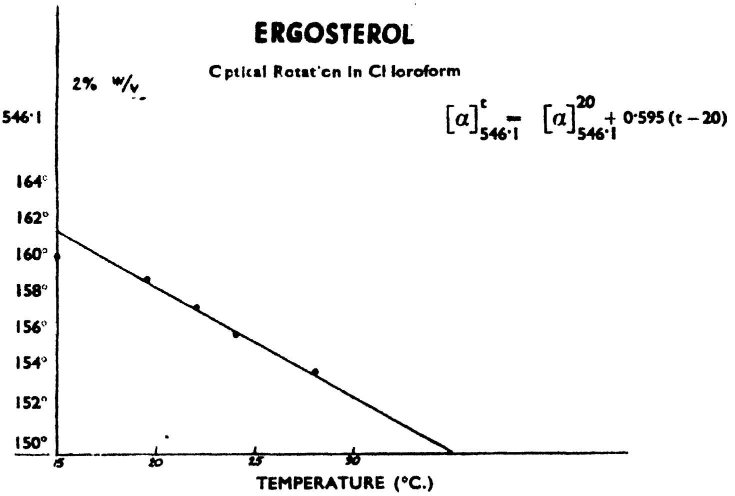

Fig. 5

In the Report of the Second International Vitamin Conference the value for the optical rotation of calciferol is given as 119° to 122°. This figure is clearly based on the figure of 122°, given by Askew *et al.*[7] We have in this matter had the valuable advice of Dr. R. K. Callow[8]; he has fortunately been able to confirm our observations as to the effects of temperature and concentration on the optical rotation of calciferol, and is of opinion that the original value assigned to it was too low.

RELATION BETWEEN ABSORPTION AND ROTATION.—The samples examined during the last two years comprise 73 different batches of calciferol. Fig. 6 is a scattergraph showing the relation between ultra-violet absorption and optical rotation, determined at the standardised temperature and concentration. It appears to show complete scatter—strong presumptive evidence that all variations are due to experimental error and not to the presence of any particular impurity. A similar complete scatter is shown when the figures for the specific absorption are tabulated year by year as shown in Fig. 7. In spite of the relatively small number of observations, the distribution of the values in each year begins to approximate to those of a normal frequency curve.

The average for the determinations in 1935 and 1936 is 477. When allowance is made for an experimental error of observation amounting to ±2·5 per cent., the range is 465 to 489. About one-third of the figures fall outside this range.

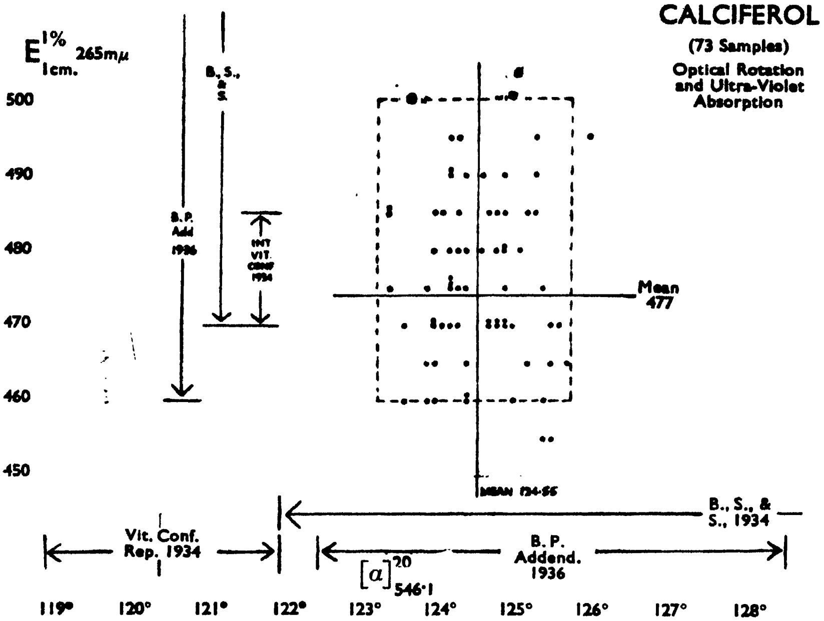

Fig. 6

The average figure for the rotation of the 73 samples in 1935 and 1936 is +124·55°. Since the polarimeter used can be read with a precision of ±0·02°, the deviation from the mean due solely to observational error would, for a substance with a rotation of 125°, determined in a 4-decimetre tube at a concentration of 4 per cent., be only ±0·125°. This is quite insufficient to explain the range of values encountered, the great majority of which fall outside these limits.

In Fig. 8 we show the whole of the values for ultra-violet absorption and optical rotation of the 73 samples; these values are also arranged towards the right of each graph to show their frequency distribution. Those for the absorption would fall on a steeper curve than those for the rotation, but here also there are indications of a trend towards normal distribution.

It so happens that we have some kind of check on the accuracy of determining both specific absorption and specific rotation. Owing to the time and expenditure involved in biological assay it is not our custom to estimate by this means the biological activity of each batch of calciferol separately. Groups of four, five or six batches, according to convenience, are blended together with great thoroughness, and a sample of the blend is used for biological assay. The specific absorption and specific rotation of these blended samples is also always determined, and can

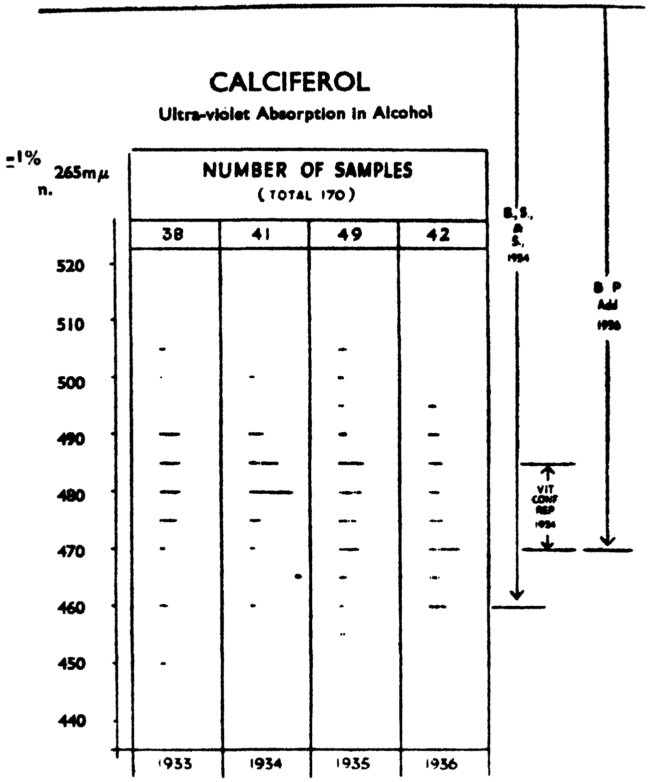

Fig. 7

therefore be compared with the values obtained by calculation, with proper weighting, from the individual batches in the blend. It appeared that there

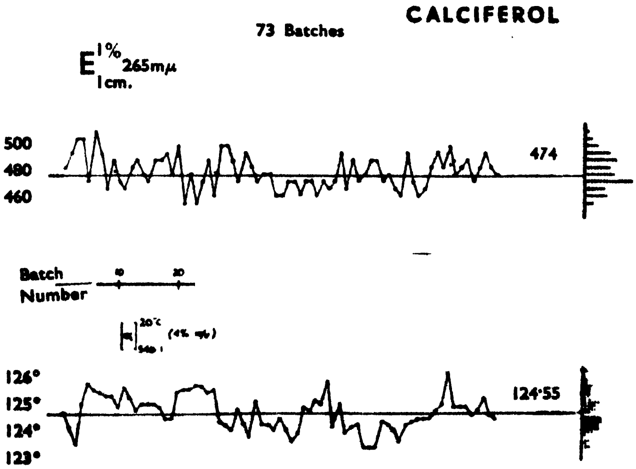

Fig. 8

was frequently a marked difference between those found and those calculated. There is no correlation between the differences found for the rotation and those found for the absorption; they cannot be accounted for by inadequate blending, but must rather be ascribed to inherent errors of determination. The differences between the found and calculated figures for both values are shown in Table II; the maximum differences transcend by very little the departures from the average shown by individual batches, with a few outstanding exceptions.

These figures suggest strongly to us that the limits of observational error in determining the ultra-violet absorption, and especially the optical rotation of calciferol, have been fixed too low. The departures of the two sets of values found from those calculated are such as to indicate that errors of determination may be of the order of ±15 (±3 per cent.) for absorption and ±0·5° (±0·4 per cent., corresponding with a reading of ±0·08°) for rotation. With such errors, 17 out of 73 values for absorption and 34 values for rotation still fall outside the expected limits.

TABLE II

		$[\alpha]^{20}_{546\cdot1}$ 4 per cent. w/v in absolute alcohol		$E^{1\%}_{1\,\text{cm.}}$ 265$m\mu$	
Blend	No. of batches	Found	Calculated	Found	Calculated
I	8	124·9°	124·9°	480	483
II	4	125·2°	125·4°	460	465
III	5	124·5°	124·8°	480	486·5
IV	4	124·4°	124·5°	480	481·5
V	6	123·9°	124·1°	470	467
VI	5	125·0°	125·0°	480	467·5
VII	6	124·2°	124·1°	475	474
VIII	6	124·5°	123·8°	465	473·5
IX	6	124·4°	124·4°	495	477·5
X	4	124·3°	124·9°	470	482·5
XI	5	124·0°	124·3°	480	481·5

Difference.	Maximum + ..	0·6 (0·10°)*	+12·5 (2·5 per cent.)
	Maximum − ..	0·7 (0·112°)*	−17·5 (4 ,,)
	Average (neglecting signs) ..	0·23 (0·04°)*	7·5 (1·5 ,,)

* Actual reading (in parentheses).

We have no explanation at present to offer for these departures from the normal behaviour of "pure" compounds, of which we believe calciferol to be one. At least, however, we think we have reduced the systematic errors of determination to below those previously encountered.

BIOLOGICAL ACTIVITY.—The biological activity of the eleven blends examined is shown in Table III. Taking into consideration the number of pairs of animals used for the test in the manner recently described by a Sub-Committee of the Pharmacopoeia Commission,[9] the values all fall within the expected limits for a substance having an activity of 40 million units per gram.

TABLE III

Blend	Animals (No. of pairs)	International units (per microgram)
I	14	40
II	8	>40
III	11	>40
IV	6	40
V	10	40·5
VI	16	39·5
VII	9	41·2
VIII	11	43·4
IX	13	44·5
X	23	35·7
XI	13	45·0
Weighted mean (134 pairs)	..	40·8

CONCLUSIONS.—The 73 samples of calciferol, whose physico-chemical properties are here reviewed, represent the result of carefully controlled and highly standardised conditions of manufacture. The product would be expected to show the constancy of properties associated with a single pure chemical compound.

TABLE IV

CALCIFEROL (73 SAMPLES)

	$E^{1\%}_{1\,\mathrm{cm.}}$ 265$m\mu$	$[\alpha]^{20}_{546\cdot1}$ $(c=4\cdot0)$
Range	455 to 505	123·4° to 126°
Mean	477	124·55°
Maximum deviation from mean ..	+30	+1·45°
Proposed limit	480 ± 20 (460 to 500)	124·5 ± 1·3° (123·2° to 125·8°)

The melting-point is as constant as can be expected in a substance that decomposes at its melting-point. Nearly eighty per cent. of the figures for specific absorption in the ultra-violet region fall within the range anticipated on the basis of ascertained experimental error. Forty-five per cent. of the figures for optical rotation show a range outside what would be similarly expected, and for these deviations we have at present no explanation. In spite of the unexplained

TABLE V

CALCIFEROL

	Bacharach, Smith and Stevenson 1933	International Vitamin Conference 1934	B.P. Addendum 1936	Anderson, Bacharach and Smith 1937
Melting-point ..	115° to 117° C.	114·5° to 117° C.	115° to 119° C.	unsharp, 116° C.
$[\alpha]^{20°}_{546\cdot1}$ (in alcohol)	> +122°	+119° to +122°	*+122·5° to +128·5°	*+123·25° to +125·75°
$E^{1\%}_{1\,\mathrm{cm.}}$ 265$m\mu$ ..	not <470	470 to 485	not <460	460 to 500

* 4 per cent. solutions w/v.

deviations, all the samples fall well within the range laid down in the 1936 Pharmacopoeial Addendum,[3] and that range is, in our opinion, unnecessarily wide.

We therefore propose a revised specification for pure calciferol based upon the findings summarised in Table IV. For purposes of convenience our proposed new specification is compared in Table V with our own earlier specification, as well as with those put forward by the 1934 International Conference on Vitamin Standardisation[2] and in the 1936 Pharmacopoeial Addendum.[3]

We wish to take this opportunity of expressing our thanks to the analytical department of these laboratories upon whose many observations of optical rotation and specific absorption this paper is largely based. We would particularly acknowledge the assistance of Miss M. Finlayson and Miss G. M. Adlington (Mrs. G. M. White).

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Mannich's Method for the Determination of Morphine

BY JOHN RALPH NICHOLLS, B.Sc., F.I.C.

MANNICH, Handke and Baumgarten[1] describe a process for the quantitative determination of morphine by precipitation as the 2:4-dinitrophenyl ether. The precipitation is carried out in aqueous methyl alcohol solution, sodium or potassium hydroxide being used to bring about the reaction between morphine and 1:chloro-2:4-dinitrobenzene.

In an examination of the method it was found that the proportion of alkali used was critical and that an excess over a certain amount caused the solutions to darken considerably in colour (owing to the decomposition of the chlorodinitrobenzene) and decreased the sensitivity when applied as a test for small quantities of morphine. For example, when equal quantities of a dilute morphine solution were treated as described by Mannich, but with varying concentrations of alkali, precipitates formed in solutions having alkalinities up to 0·02 N (calculated on the whole solution) within 2 hours, but solutions of higher alkalinities showed no precipitate within that time. In working with extracts of opium it was difficult to ensure the correct degree of alkalinity. In addition, with pure morphine the conditions specified by Mannich did not yield quantitative results, the solubility of the ether being approximately 4 mg. per 100 ml.

The method, however, appeared sufficiently promising to warrant further study, and it was found that when the precipitation was carried out in about 30 per cent. ethyl alcohol solution (instead of in aqueous methyl alcohol) and a considerable quantity of ammonia (instead of fixed alkali) was used, quantitative results could be obtained with very little, if any, decomposition of the reagent.

APPLICATION OF THE MODIFIED METHOD TO MORPHINE SALTS.—Solutions containing known amounts of pure morphine dissolved in $N/10$ acid were diluted with water to 60 ml., and 25 ml. of alcohol (95 per cent.), 10 ml. of strong ammonia solution and 5 ml. of a 2 per cent. solution of 1:chloro-2:4-dinitrobenzene in alcohol (95 per cent.) were added to each and well mixed. After standing overnight (18 hours) each was filtered through a tared Gooch crucible packed with asbestos, the precipitate and flask being washed with 30 per cent. alcohol and finally with a little ether to remove any traces of chlorodinitrobenzene. The crucible was dried at 100° C. and weighed. The results obtained are given in the following table:

Anhydrous morphine present g.	Weight of ether obtained g.	Anhydrous morphine (ether × 0·632) g.
0·0716	0·1132	0·0715
0·0294	0·0464	0·0293
0·0029	0·0046	0·0029
0·00074	0·0012	0·00076

With greater concentrations of morphine, precipitation was not complete in 18 hours, possibly owing to insufficient excess of chlorodinitrobenzene. The quantity of this reagent that can be usefully added is limited by its solubility in the 30 per cent. alcoholic solution.

The conditions applicable to morphine salts may be summarised as follows:—Dissolve a weighed quantity of the morphine salt in 30 per cent. alcohol. To every 100 ml. of solution, which must not contain more than 0·1 g. of morphine salt, add 10 ml. of strong ammonia solution and 5 ml. of a 2 per cent. solution of 1:2:4-chlorodinitrobenzene in alcohol (95 per cent.). Allow the mixture to stand for 18 hours, filter through a tared Gooch crucible, and wash the precipitate with 30 per cent. alcohol and finally with a little ether. Dry the precipitate at 100° C. and weigh. Multiply the weight of the precipitate by 0·632 to obtain anhydrous morphine.

These conditions can be employed for certain mixtures containing morphine salts; but it must be remembered that other phenolic alkaloids may give insoluble ethers with chlorodinitrobenzene.

APPLICATION TO OPIUM.—It was found that opium extracts, prepared as described by Mannich and precipitated under the modified conditions given above, yielded precipitates of different colour from those given by morphine salts, the shades varying from yellow to brown. An additional small error was introduced by the fact that after precipitation of the calcium from the lime water extract of opium by means of potassium oxalate the addition of the necessary alcohol yielded a further small precipitate of calcium oxalate. The former of these difficulties was overcome by treating the opium extracts with lead acetate, and the latter by precipitating the calcium in 30 per cent. alcoholic solution. A convenient treatment of opium was as follows:

Two or five g. of opium were completely extracted with successive portions of water, and the solutions were filtered through a sintered glass funnel and diluted to 100 or 250 ml., respectively. To 75 ml. of the solution were added 0·5 g. of powdered lead acetate and, when this had dissolved, 0·5 g. of calcium hydroxide, and the mixture was well shaken and filtered through a fluted filter-paper. To 50 ml. of the filtrate (equivalent to 1 g. of opium) were added 1 g. of oxalic acid and 30 to 35 ml. of alcohol (95 per cent.) and the mixture was allowed to stand for an hour and then diluted to 100 ml. with water. After filtration, an aliquot part of the filtrate was treated as specified above.

Alternatively, 1 g. of opium was ground into a sludge with 0·5 g. of lead acetate and a little water, and then mixed with 0·5 g. of calcium hydroxide. The mixture was filtered on a sintered glass funnel, and the residue was re-ground with water and filtered. The process was repeated until the opium was completely extracted, yielding about 80 ml. of filtrate. To the filtrate were added 1 g. of oxalic acid and sufficient alcohol to yield approximately 30 per cent. in the solution. After being shaken and allowed to stand, the mixture was filtered, and the residue was washed with 30 per cent. alcohol. An aliquot part of the filtrate was treated in the same way as for morphine.

In every instance several tests were carried out with the same volume of solution for precipitation, but with varying concentrations of opium extract. It was found that the smaller concentrations gave lower results than the larger, not on account of solubility, but owing, at least in part, to a slower rate of precipitation; if the mixtures were allowed to stand for longer than 18 hours, in some cases 4 days, the results were approximately the same. Examination of the precipitates showed, however, that they were not the pure morphine ether; when tested by Zeisel's method they all yielded silver iodide, indicating the presence of methoxy groups, which are not present in morphine. The weights of silver iodide obtained from 0·1 g. of ethers derived from different varieties of opium varied from 0·0012 to 0·0077 g. Ethers obtained from opium extracts from which the non-phenolic alkaloids had been exhaustively extracted still contained methoxy groups, showing that other phenolic alkaloids in opium give insoluble ethers in the same way as morphine. Assuming that these interfering alkaloids contain, like laudanine, three methoxy groups, the morphine calculated from the weight of ether produced may be up to 6 per cent. too high, *i.e.* 0·6 per cent. on 10 per cent. of morphine. If the interfering alkaloids have one or two, instead of three, methoxy groups, the error is proportionately greater.

The Mannich method is, therefore, unsatisfactory for the accurate assay of opium.

SUMMARY.—1. Mannich's method has been modified to give quantitative results for the assay of morphine in its salts.

2. The method, whether modified or not, does not give accurate results with opium, since other phenolic alkaloids present in opium yield insoluble ethers under the same conditions.

I wish to thank Dr. J. J. Fox, Government Chemist, for permission to publish this work.

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GOVERNMENT LABORATORY
LONDON, W.C.2

The Determination of Potassium as Potassium Silver Cobaltinitrite

BY A. M. ISMAIL, PH.D., AND H. F. HARWOOD, M.SC., PH.D., F.I.C.

VARIOUS difficulties have been encountered in the application of the Kramer and Tisdall cobaltinitrite method to the determination of potassium in soil solutions. Furthermore, most modifications of this method give 0·10 mg. of potassium as the smallest amount that can be satisfactorily determined.

In recent work it became necessary to determine as little as 0·01 mg. of potassium, so that either an entirely new method had to be found, or a suitable modification of the cobaltinitrite process devised.

A new qualitative test for potassium was described by Kamm and Burgess[1]:—By the addition of sodium cobaltinitrite to a potassium solution containing silver ions an extremely insoluble orange-yellow precipitate of potassium silver cobaltinitrite is produced. An analogous reaction, depending on the formation of a potassium lead cobaltinitrite, was proposed by Tovarnitzki and Sergienko[2]; in this case the potassium was determined by a volumetric method, as in the ordinary cobaltinitrite process.

The use of such reagents as those mentioned above is attractive, as the compounds formed by them have a high molecular weight, and small amounts of potassium would thus yield considerable weights of precipitate, leading to an increased accuracy in the determination.

A comparative test of the above reagents showed that the sodium silver cobaltinitrite afforded the most delicate test; thus

Volume of Solution 0·5 ml.

Potassium mg.	Sodium cobaltinitrite	Sodium lead cobaltinitrite	Sodium silver cobaltinitrite
1·0	Immediate ppt.	Immediate ppt.	Immediate ppt.
0·5	,, ,,	,, ,,	,, ,,
0·1	,, ,,	,, ,,	,, ,,
0·05	,, opalescence	,, opalescence	,, ,,
0·01	No visible change	No visible change	,, turbidity

Attempts were accordingly made to establish a micro-method for the determination of potassium based on the formation of potassium silver cobaltinitrite.

The first difficulty encountered was due to the fine state of division of the potassium complex, and its tendency to pass into the colloidal state. Although, on standing in the liquid, the precipitate settled out—still more rapidly if the solution were centrifuged—yet when it was washed with water and centrifuged, the difficulty in separating the precipitate increased with each successive washing, so that after the third treatment it was practically impossible to effect a complete separation. The use of solutions of electrolytes, such as sodium nitrate, sulphate or acetate, as washing liquids was tried, but without an improved result. Finally, a method of overcoming the difficulty was reached by precipitating the potassium complex in an alcoholic or acetone medium; the particles of the complex formed were coarser, the precipitate coagulated and settled quickly, and the time of centrifuging was also considerably shortened. The most suitable concentration of alcohol or acetone for the precipitating medium was 20 per cent. Acetone proved preferable to alcohol, and was accordingly adopted throughout. Washing the precipitate with 50 per cent. acetone more than once was not satisfactory, as the wash liquid in the second and subsequent washings acquired a slight opalescence; 80 per cent. acetone was accordingly used for the second and later washings. Tests showed that the first washing of the complex with 50 per cent. acetone removed the excess of the sodium silver cobaltinitrite reagent almost completely, whilst the second and third washings, with 80 per cent. acetone, eliminated the last traces. The next point was whether the precipitate of the double cobaltinitrite of silver and potassium obtained under the ordinary working conditions would be constant in composition. Kamm and Burgess[1] stated that the colour of the precipitate varies from yellow to orange, this being in accordance with the conditions of precipitation, that its composition also appears to be dependent upon these conditions, and that the larger the excess of silver present in the original solution the more will be found in the precipitate. No attempt has been made to prove or disprove the last statement, because of the impossibility of effecting a quantitative separation of the complex from aqueous solution under the qualitative conditions obtaining in Kamm and Burgess's experiments. As will be shown later, the potassium complex obtained by the method to be described proved to have a constant composition.

To investigate the constancy of composition of the complex, varying quantities of potassium were precipitated, and the silver-content of the washed precipitate was determined. As the result of a series of trials, the following procedure was established as the most suitable for the precipitation of potassium in the form of potassium silver cobaltinitrite:

Two ml. of the potassium solution (free from halogens, and containing from 0·15 to 2·0 mg. of potassium) are placed in a centrifuge tube and acidified with one drop of glacial acetic acid. One ml. of 0·7 per cent. silver nitrate solution is added, and the solutions are well mixed with a thin glass rod. One ml. of 80 per cent. acetone is then gradually added, the liquid being well mixed after each addition. The tube, together with the glass rod, is left in an ice-bath for 5 minutes, and 1 ml. of 25 per cent. sodium cobaltinitrite solution (freshly prepared and cooled in an ice-bath for 5 minutes) is added, drop by drop, with stirring after each addition. After 0·9 ml. of the reagent has been added, the glass rod is allowed to drain and is rinsed with the remaining 0·1 ml., and the tube is left in the ice-bath for 2 hours, after which it is centrifuged for 3 minutes at 3000 r.p.m. The supernatant liquid is decanted, and the tube is inverted and left to drain, its mouth and upper part being subsequently wiped with a small piece of filter-paper. About 3 ml. of 50 per cent. acetone are run in, down the sides of the tube, in small quantities at a time, with gentle agitation after each addition; care must be taken that the precipitate is disturbed as little as possible. The tube is then centrifuged for 2 minutes, the liquid is decanted, and the tube is inverted as before to drain. This treatment removes the excess of the reagent with the exception of that adhering to the precipitate. About 3 ml. of 80 per cent. acetone are now run in down the side of the tube, and the precipitate is stirred with the glass rod, which is then allowed to drain, and rinsed with 2 ml. of 80 per cent. acetone. The tube is then centrifuged for 3 minutes, the liquid is decanted, and the tube is inverted to drain. The washing with 80 per cent. acetone must be repeated twice more, otherwise a trace of soluble silver salt remains with the precipitate.

TABLE I

No.	Potassium taken mg.	0·01 *N* ammonium thiocyanate used in titration ml.	Ratio $\frac{\text{Ml. of ammonium thiocyanate}}{\text{Mg. of potassium}}$
1	2·00	4·150	2·075
2	2·00	4·160	2·080
3	1·70	3·520	2·071
4	1·70	3·510	2·065
5	1·50	3·090	2·060
6	1·50	3·095	2·063
7	1·40	2·890	2·064
8	1·40	2·880	2·057
9	1·30	2·675	2·058
10	1·30	2·675	2·058
11	1·15	2·360	2·052
12	1·15	2·370	2·061
13	1·00	2·060	2·060
14	1·00	2·070	2·070
15	0·90	1·850	2·056
16	0·90	1·855	2·061
17	0·75	1·535	2·047
18	0·75	1·540	2·053
19	0·60	1·230	2·058
20	0·60	1·235	2·056
21	0·45	0·925	2·056
22	0·45	0·925	2·056
23	0·30	0·615	2·050
24	0·30	0·615	2·050
25	0·20	0·410	2·050
26	0·20	0·415	2·075
27	0·20	0·410	2·050
28	0·15	0·305	2·033
29	0·15	0·310	2·067
30	0·15	0·310	2·067

DETERMINATION OF SILVER IN THE POTASSIUM COMPLEX.—Four ml. of dilute (1:4) nitric acid are run into the centrifuge tube containing the washed precipitate, and the tube is left in a boiling water-bath until the precipitate is completely decomposed and all nitrous fumes have been expelled. After cooling, 0·5 ml. of ferric alum solution is added, and the silver is determined by titration with 0·01 *N* ammonium thiocyanate by means of a 5-ml. micro-burette which can be read to 0·01 ml. The results of a number of experiments in which a standard solution of potassium nitrate was used are given in Table I.

From these figures it is evident that the method yields consistent results, and that the potassium silver complex obtained from different initial quantities of potassium has a constant composition, as the duplicate determinations agree among themselves, and the ratio of the titration figures to the amount of potassium present is reasonably constant. Consequently, an equivalent for the ammonium thiocyanate solution may be calculated from the mean of a number of the results, the value so obtained being 1 ml. of 0·01 *N* thiocyanate = 0·4878 mg. of potassium.

Using this equivalent, the previous figures can be recalculated as shown in the following table (Table II):

TABLE II*a*

STANDARD POTASSIUM NITRATE SOLUTION

No.	Potassium taken mg.	Thiocyanate used ml.	Potassium found mg.	Difference mg.
1	2·00	4·150	2·024	+0·024
2	2·00	4·160	2·029	+0·029
3	1·70	3·520	1·717	+0·017
4	1·70	3·510	1·712	+0·012
5	1·50	3·090	1·507	+0·007
6	1·50	3·095	1·510	+0·010
7	1·40	2·890	1·410	+0·010
8	1·40	2·880	1·405	+0·005
9	1·30	2·675	1·305	+0·005
10	1·30	2·675	1·305	+0·005
11	1·15	2·360	1·154	+0·004
12	1·15	2·370	1·156	+0·006
13	1·00	2·060	1·005	+0·005
14	1·00	2·070	1·019	+0·019
15	0·90	1·850	0·902	+0·002
16	0·90	1·855	0·905	+0·005
17	0·75	1·535	0·749	−0·001
18	0·75	1·540	0·751	+0·001
19	0·60	1·230	0·600	nil
20	0·60	1·235	0·602	+0·002
21	0·45	0·925	0·449	−0·001
22	0·45	0·920	0·451	+0·001
23	0·30	0·615	0·300	nil
24	0·30	0·615	0·300	nil
25	0·20	0·410	0·200	nil
26	0·20	0·415	0·205	+0·005
27	0·20	0·410	0·200	nil
28	0·15	0·305	0·149	−0·001
29	0·15	0·310	0·151	+0·001
30	0·15	0·310	0·151	+0·001

As with very small quantities of potassium (less than 0·10 mg.) the titration figures for the silver-content are unduly small, it was found advisable to add 1 ml. of 0·01 *N* silver nitrate solution to the solution of the potassium complex prior to the titration with ammonium thiocyanate.

TABLE II*b*

No.	Potassium taken mg.	Thiocyanate (Silver in ppt. + added silver) ml.	Thiocyanate (Silver-content of ppt.) ml.	Potassium found mg.	Difference mg.
31	0·10	1·205	0·205	0·100	nil
32	0·10	1·205	0·205	0·100	nil
33	0·10	1·200	0·200	0·098	−0·002
34	0·05	1·100	0·100	0·048	−0·002
35	0·05	1·100	0·100	0·048	−0·002
36	0·05	1·105	0·105	0·051	+0·001

With quantities of potassium less than 1 mg., the whole process of precipitation, washing, dissolving, and subsequent titration may be carried out in the centrifuge tube.

VOLUMETRIC DETERMINATION OF THE NITRITE GROUP IN THE POTASSIUM SILVER COMPLEX.—It became obvious at this stage of the work that the use of the titration of the silver-content of the precipitate as a means for the indirect determination of the potassium was only practicable with amounts of potassium exceeding 0·1 mg.

The possibility of determining the nitrite-content of the complex suggested itself as an alternative, since it would afford a much bigger titration figure, and render practicable the determination of very small amounts of potassium.

The direct titration of a nitrite with ceric sulphate solution, erioglaucine being employed as indicator, and the use of ceric sulphate solution in place of potassium permanganate for the determination of the nitrite-content in the potassium sodium cobaltinitrite precipitate have been examined by Bennett and Harwood.[3] The use of ceric sulphate for this purpose has the advantage of avoiding the danger of decomposition of the standard solution on boiling or heating (especially when a very dilute solution is used) which is a drawback in the customary permanganate method; the end-point of the ceric sulphate titration is also very sharp.

The determination of the nitrite group in the potassium silver complex necessitated a modification of the procedure previously given for the washing of the precipitate, as it was necessary that all acetone should be removed. This was effected in the following manner:

After the third washing of the precipitate with 80 per cent. acetone, about 3 ml. of pure acetone were run down the sides of the tube, in small portions at a time, with agitation after each addition, the precipitate being brought into a state of suspension and well stirred. The glass rod was then rinsed with 2 ml. of acetone and the tube was centrifuged for 2 minutes. The liquid was decanted, and the tube was inverted and allowed to drain and dry completely. About 3 ml. of pure ether were run in, and the tube was shaken to ensure thorough mixing of the precipitate and ether; a thin glass rod was used in some cases, the rod being left in the tube during the subsequent titration. The tube was then centrifuged for 1 minute, the ether decanted, and the tube allowed to dry.

Ceric Sulphate Titration.—The method used for the titration of the nitrite-content of the dried potassium silver cobaltinitrite was essentially the same as that described by Bennett and Harwood.[8]

TABLE III

No.	Potassium taken mg.	0·02 N ceric sulphate used in titration ml.	Potassium found mg.	Difference mg.
1	0·900	8·285	0·900	nil
2	0·900	8·285	0·900	nil
3	0·750	6·900	0·750	nil
4	0·750	6·905	0·750	nil
5	0·600	5·530	0·601	+0·001
6	0·600	5·520	0·600	nil
7	0·500	4·600	0·500	nil
8	0·500	4·605	0·500	nil
9	0·400	3·690	0·401	+0·001
10	0·400	3·680	0·400	nil
11	0·300	2·770	0·301	+0·001
12	0·300	2·760	0·300	nil
13	0·250	2·300	0·250	nil
14	0·250	2·310	0·251	+0·001
15	0·150	1·380	0·150	nil
16	0·150	1·380	0·150	nil
17	0·100	0·910	0·099	−0·001
18	0·100	0·920	0·100	nil
		0·01 N ceric sulphate used in the titration ml.		
19	0·050	0·925	0·050	nil
20	0·050	0·915	0·050	nil
21	0·030	0·560	0·030	nil
22	0·030	0·560	0·030	nil
23	0·020	0·380	0·021	+0·001
24	0·020	0·380	0·021	+0·001
25	0·010	0·250	0·014	+0·004
26	0·010	0·250	0·014	+0·004

An excess of 0·02 N ceric sulphate solution was run on to the dry precipitate in the centrifuge tube, followed by 2 ml. of 2 N sulphuric acid. The tube was then placed in a boiling water-bath until decomposition of the precipitate was complete, after which the liquid was transferred to a small Erlenmeyer flask and the tube was washed out with small quantities of 2 N sulphuric acid. The contents of the flask were heated to boiling, and cooled under the tap. An excess of 0·02 N ferrous ammonium sulphate solution was then added, and the solution was titrated with standard ceric sulphate, a 0·1 per cent. aqueous solution of erioglaucine being used as indicator.

A series of experiments with known amounts of potassium showed that perfectly concordant results were obtainable over a wide range. As a result of these, the equivalent of the ceric sulphate solution used was found to be 1 ml. of 0·02 *N* ceric sulphate solution = 0·1087 mg. of potassium. For the determination of amounts of potassium less than 0·10 mg., it was found preferable to use 0·01 *N* ceric sulphate solution for the titration; with a solution of this concentration the fading of the orange-pink colour after the end-point has been reached is more pronounced than with 0·02 *N* solution, but, despite this, the colour-change at the end-point is quite sharp. Table III gives the results obtained in a series of experiments with a standardised solution of potassium nitrate as initial substance.

From a comparison of the results in Tables II and III it will be seen that the method affords satisfactory determinations of amounts of potassium ranging from 2 mg. down to 0·03 mg., with an accuracy of about 1 per cent. Amounts of potassium down to 0·01 mg. can be determined, but the accuracy attainable with these very small amounts is considerably less. It would probably be better to carry out the determination in such cases by dissolving the precipitate and determining the nitrite by a colorimetric method.

Experiments made with a view to ascertaining the exact composition of the potassium silver complex showed that, whilst the precipitate formed under the experimental conditions described always possessed a constant composition, the compound itself could not be expressed by any simple formula. It is apparently a mixture in constant proportions of the two salts $KAg_2Co(NO_2)_6$ and $K_2AgCo(NO_2)_6$.

APPLICATION OF THE METHOD TO THE DETERMINATION OF POTASSIUM IN SOIL SOLUTIONS.—In order to ascertain whether the presence of other salts affected the determination of potassium by the potassium-silver cobaltinitrite method, a number of solutions were prepared; these contained metals generally present in soil extracts. A list of these solutions follows:

Calcium sulphate	Saturated aqueous solution
Magnesium sulphate	1 ml. = 10 mg. of magnesium
Manganous sulphate	1 ml. = 10 mg. of manganese
Ferrous sulphate	1 ml. = 10 mg. of iron
Aluminium sulphate	1 ml. = 10 mg. of aluminium
Sodium phosphate	1 ml. = 10 mg. of phosphoric oxide

Mixtures with different quantities of potassium nitrate were made from these, so that the resulting solution represented the average composition of a soil extract, and the potassium was then determined by the method previously described. The results are given in Table IV, and show clearly that the presence of the above-mentioned metals and acids is without influence on the accuracy of the potassium determination.

Preliminary Treatment of the Soil Solution.—In the application of the potassium silver cobaltinitrite method to the determination of potassium in soil solutions it is necessary to carry out a preliminary treatment of the solution to decompose organic matter and to remove ammonia and chlorides.

Evaporation of the soil solution with hydrochloric acid, nitric acid, and sulphuric acid in turn, followed by the ignition of the residue was tried, as was also Selke's digestion method,[4] which is based on the use of perhydrol to destroy organic matter with caustic soda to expel ammonia. Neither of these methods proved satisfactory, irregular results being obtained for the potassium in the subsequent determinations.

TABLE IV

Potassium taken mg.	Ca soln. mg.	Mg soln. mg.	Mn soln. mg.	Fe soln. mg.	P_2O_5 soln. mg.	Al soln. mg.	Ceric sulphate used ml.	Potassium found mg.	Diff. mg.
0·100	—	—	—	—	—	—	0·925	0·1005	+0·0005
0·050	—	—	—	—	—	—	0·475	0·0510	+0·001
0·200	1·00	1·00	1·00	1·00	1·00	1·00	1·880	0·204	+0·004
0·200	1·00	1·00	1·00	1·00	1·00	1·00	1·820	0·198	−0·002
0·100	0·50	0·50	0·50	0·50	0·50	0·50	0·930	0·101	+0·001
0·100	0·50	0·50	0·50	0·50	0·50	0·50	0·930	0·101	+0·001
0·050	0·25	0·25	0·25	0·25	0·25	0·25	0·455	0·050	nil
0·050	0·25	0·25	0·25	0·25	0·25	0·25	0·470	0·051	+0·001

The following method for the preliminary treatment of the soil solution was finally worked out, and yielded quite satisfactory results:

Procedure.—Five ml. of the soil solution are pipetted into a small dish with a good glazed surface, and mixed with an equal volume of conc. nitric acid, and the solution is evaporated to dryness. The residue is taken up with 3 ml. of water, a further 5 ml. of conc. nitric acid are added, and the evaporation to dryness is repeated. The dish is then covered with a watch-glass and heated first for 30 minutes in an air-oven at 130°–140° C., and then over a small flame, being held with a pair of platinum-tipped tongs and kept moving above the flame to prevent local overheating. When no further odour or charring is perceptible, the residue in the dish, brown at first, but now lighter in colour, is extracted with 2 to 3 ml. of hot water, solution being aided by stirring with a short glass rod. The contents of the dish are carefully heated to boiling, and, after cooling, the liquid is filtered through a 7-cm. Whatman No. 40 filter into a centrifuge tube. The dish is washed with small quantities of water, and the washings are passed through the filter. The solution in the tube is then evaporated to 2 ml., and one drop of glacial acetic acid is added. The contents of the tube are now ready for the determination of potassium, which is carried out in the manner previously described.

The following tables (V and VI) show the results thus obtained with a number of different soil solutions. It will be seen that the duplicates agree well among themselves, and that when known amounts of potassium had been added to the soil solution its recovery was satisfactory.

The agreement between the amounts of potassium found when different volumes of the same soil solution are used is satisfactory, considering the small quantities involved. Previous workers have experienced considerable difficulties in this respect when using the older method, finding that although reproducible results could be obtained with similar volumes of soil solution, wide variations resulted when different initial volumes were taken. This point was especially noted by Dixon,[5] who found that when using a combination of Selke's perhydrol pre-treatment process with the Kramer–Tisdall cobaltinitrite method, although the results with pure potassium chloride solutions agreed well with one another, he was quite unable to obtain good results when the process was applied to actual soil extracts, variations of as much as 50 per cent. resulting when different initial volumes of soil solution had been taken.

TABLE V

SOIL SOLUTION WITH ADDED POTASSIUM

Sample	Soln. taken ml.	Potassium added mg.	Total potassium found mg.	Potassium in soil soln. taken* mg.	Added potassium recovered mg.	Difference mg.
1	3	nil	0·063	—	—	—
1	3	nil	0·062	—	—	—
1	3	0·100	0·160	0·062	0·098	—0·002
1	3	0·100	0·158	0·062	0·096	—0·004
1	6	nil	0·128	—	—	—
1	6	0·100	0·228	0·128	0·100	nil
1	9	nil	0·188	—	—	—
1	9	0·100	0·287	0·188	0·099	—0·001

* These are the "blank" values from the preceding column.

TABLE VI

SOIL SOLUTION ALONE

Sample	Soil solution taken ml.	Potassium found mg.
2	3	0·050
2	3	0·050
2	6	0·102
2	6	0·101
2	9	0·152
2	9	0·153
3	5	0·036
3	10	0·065
4	2	0·190
4	2	0·193
4	3	0·283
4	3	0·283
5	5	0·128
5	5	0·129
6	10	0·168
6	10	0·165
7	2	0·020
7	4	0·044
7	6	0·063
7	8	0·082
8	2	0·234
8	4	0·451
8	6	0·698
8	8	0·907

The method described in this paper has been used by several research workers in the Agricultural Chemistry Department of the Imperial College in order to ascertain its suitability for general use in the determination of small amounts of potassium in soil extracts; it has been found to yield very satisfactory results—better than are obtainable by the usual sodium cobaltinitrite method.

The work here described was begun in October, 1934, and completed in June of the following year. In the interim a paper has been published by Robinson and Putnam[6] on the determination of potassium in waters. These workers have arrived independently at a somewhat similar method, also precipitating the potassium as the double silver potassium cobaltinitrite in the presence of acetone. The subsequent treatment of the precipitate differs from that given in this paper, the nitrite-content of the precipitate being determined by a colorimetric process.

In conclusion, we desire to express our indebtedness to Mr. L. S. Theobald, of the Imperial College, for suggesting the suitability of the double potassium silver cobaltinitrite for use in potassium determinations.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
SOUTH KENSINGTON, S.W.7

The Hartridge Reversion Spectroscope for the Examination of Blood for Carbon Monoxide; Improvements in Design, Assembly and Technique

BY ROBERT C. FREDERICK, F.I.C.

(Read at the Meeting, April 7, 1937)

THIS spectroscope was devised by Professor Hartridge, primarily for the purpose of examining blood for carbon monoxide. In a previous paper[1] I have discussed poisoning by this gas, and have described the manipulation of the instrument in detail; by its means it is possible not only to detect carbon monoxide but to determine the amount present. The gas combines with the haemoglobin to form carboxyhaemoglobin, the two absorption bands of which are more towards the violet end of the spectrum than those of oxyhaemoglobin, and this displacement is related to the percentage saturation of the blood with carbon monoxide. But the difference is not large, and can only be measured with an instrument of precision. In the Hartridge Reversion Spectroscope, by employing two spectra in reverse directions, the effect is doubled, and in consequence carbon monoxide can be determined even when present only in small amount.

The improvements to be described have been made with a view to increasing the sensitiveness of the instrument still further, and to facilitate its operation. The modified spectroscope* (Fig. 1) has not been altered fundamentally in design; the apparent radical alteration, if comparison is made with the figure shown in the earlier paper, is due to the fact that the products of (it is understood) the only two firms concerned in its manufacture have always exhibited this different appearance.

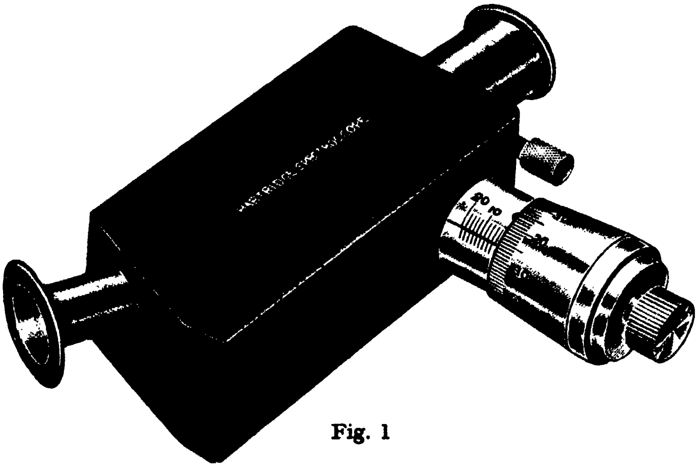

Fig. 1

The modifications which have been made in the internal arrangement of the instrument have increased the spectra very much in height, and therefore the absorption bands are viewed correspondingly elongated. As the accuracy of each reading depends upon the exactitude with which the one alpha band is brought into alignment with the other by means of the micrometer, the increased height of the bands enables this adjustment to be made more closely.

The precision that can be attained in this alignment depends also upon the character of the absorption bands; the more the aperture of the instrument is stopped down, the wider are the bands and the straighter are their edges. In this make of instrument the aperture was a fixed setting, and a screw has now been fitted to operate the slit behind the collecting lens; to compensate for this being closed to a greater degree than previously, the illumination has been increased by substituting a lamp of 150 watts in the new assembly (Fig. 2) for that of 60 watts used hitherto. The screw referred to above must on no account be moved once the examination of a sample has been begun, and should not require to be touched once the optimum conditions have been found.

The illuminating unit and other components of the assembly are mounted on a miniature table, so that the eyepiece is at a convenient level for the seated observer and, to prevent light from the unit reaching the eye, the ground-glass opening is circular, and only of such size that it is completely covered by the cell containing the diluted blood. In the assembly illustrated the table has fixed legs, but an alternative model with folding legs is available.

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* Manufactured by R. & J. Beck, Ltd., 69, Mortimer Street, London, W.1.

The zero of the micrometer, instead of being on top of the spindle, is turned towards the eyepiece, so that the observer can take a reading without moving his position. The readings are as the wave-length positions in the spectrum, so that the difference between a normal blood and one containing carbon monoxide is that the latter gives a lower reading. As the instrument should be used in a dark-room, a lamp has been placed in the electric circuit to illuminate the micrometer; to avoid distraction when making an adjustment, this is switched on and off each time a reading has to be made, and to avoid transitory impairment of visual acuity being caused by glare, the lamp is completely hooded.

The instructions that have been given for using the spectroscope specify that ten readings should be made of a normal blood, followed by an equal number of the sample under examination, and the average of each set taken. I have found that increased accuracy is obtained by alternating single readings of the normal and sample specimens until the total number required has been recorded. To facilitate this, a sliding twin cell holder has been provided; the appropriate cell is placed in the positions engraved in white "Normal" and "Sample," respectively. If carbon monoxide is not present in a sample, it should be possible to arrive at a definite conclusion with only a few readings.

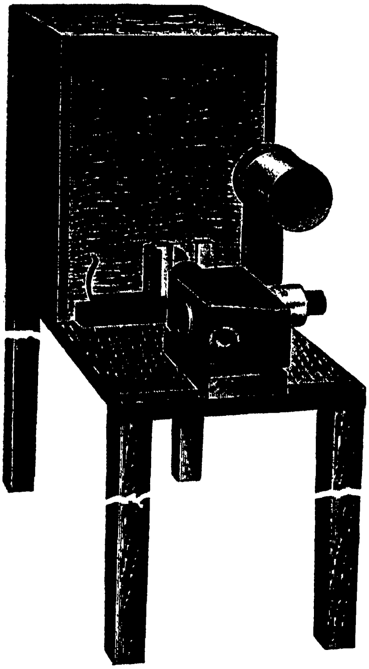

Fig. 2

In making an adjustment the alpha bands should first be thrown completely out of alignment without looking at the field, then with the eye close to the eyepiece, and the right elbow firmly placed, the micrometer screw should be turned too far, and immediately brought back to the objective position. It is an advantage to rest the eye for a few seconds between successive readings.

For the preparation of the specimens, small pieces of thin glass of the same dimensions as those of the top of a cell should be available. When the correct dilution of the blood has been reached, a minute drop of the specimen is placed on each of the shoulders of the cell, and the glass is then laid on top; this provides a seal which soon becomes firmly attached. The cells should be left in the dark for an hour or more to allow the contents to clarify by sedimentation before being examined in the spectroscope.

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ROYAL NAVAL MEDICAL SCHOOL
ROYAL NAVAL COLLEGE
GREENWICH, LONDON, S.E.10

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SOME USES OF SHEET VISCOSE IN MICROBIOLOGICAL TECHNIQUE

SHEET viscose, *e.g.* "cellophane," is now available in many colours, thicknesses and textures, and can also be obtained in moisture-proof form. In the laboratory, as elsewhere, such a material finds numerous uses. The following notes describe three microbiological applications of the colourless, non-moisture-proof variety.

I. FOR THE MICROSCOPIC EXAMINATION OF FUNGI.—The identification of mould-fungi depends largely upon the structure of the delicate sporing heads. These may be examined under a low power by removing the lid from a petri dish culture, and examining the culture directly with the aid of a microscope. Further study under a 1/6 inch or 1/12 inch objective is almost always required, however, and this presents difficulties. A little of the culture may be picked off with a sterile needle, transferred to a drop of mounting medium, and examined under a cover-slip; this method may suffice, but delicate structures are often broken up by the handling.

Growing the culture on a film of agar medium on a glass slide avoids some of the handling, but the agar film forms a bad background for microscopic examination, and gives a messy stained preparation. The same applies to "hanging drop" cultures grown under a cover-slip and in a small closed chamber; moreover, many organisms do not develop normally in a limited air supply. The method of Vernon[1] (1931), in which the fungus is grown in a channel passing across a thin agar disc surmounted by a cover-slip, is excellent for certain organisms.

The viscose modification here suggested employs, in place of agar films, small ½-in. squares of thin viscose sheet previously sterilised in the autoclave. At the time of inoculation with the fungus to be examined, the squares (say, about ten) in one petri dish are moistened with one drop each of a suitable liquid medium and inoculated, and the lid of the dish is replaced. The dish is then incubated, and from time to time a square is removed, mounted under a cover-slip in lactophenol and cotton blue medium,* or other preferred mounting medium, and examined microscopically.

The development of the fungus can thus be followed, little handling being involved, and a large number of preparations are obtained at the expenditure of very little apparatus and manipulation.

II. FOR THE STUDY OF SPORE GERMINATION.—The method described in the previous section affords an opportunity of securing preparations showing all stages in spore germination. It may also be adapted for finding the minimum humidity at which spore germination can take place—often a point of great practical importance in connection with storage problems.

Sheets of thin viscose are soaked in a suitable dilute liquid medium and air-dried. Half-inch squares cut from the prepared sheet are then suspended by loops of thread in stoppered glass jars of about 500 ml. capacity, each of which contains about 30 ml. of a suitable humidity solution, giving a range of relative humidities from 70 to 100 per cent. The solutions may be saturated solutions of appropriate salts, or sulphuric acid solutions of appropriate strength.

The bottles are incubated for some hours for the viscose to come into equilibrium with the new atmosphere, and then the squares are quickly inoculated with a streak of dry spores of the fungus under examination. The incubation period, or latent period for germination, is determined by removing a square from time to time and examining it under the microscope to see when an appreciable number of spores have begun to germinate. A square, once removed, should not be returned to the humidity jar, and can be retained for later examination or a permanent record by mounting it under a cover-slip in a drop of lactophenol and cotton blue medium.

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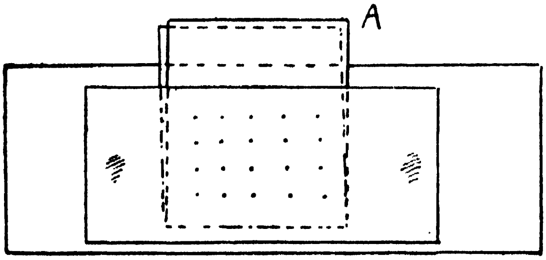
* Lactic acid 20 g., phenol 20 g., glycerin 40 g., water 20 g. and cotton blue 0·05 g.

The method has been fully described elsewhere (Galloway,[2] 1935); the minimum relative humidity for germination has been found to range from 75 to 100 per cent. for different species of fungi.

III. For the Isolation of Single Spore Cultures.—The isolation of pure cultures was made much easier when Koch (inspired, it is said, by a lady's enquiries about mould growth on jellies) introduced the method of plate cultures. Repeated plating is still the most convenient and safest method of obtaining a single spore culture, but the modern worker often wishes to see that single spore with his own eyes. Many methods have been recommended, some employing very expensive micro-manipulators, but the following viscose method has been found to work quite well, provided the spores are not too minute.

Reference to the accompanying diagram will make the method clear. A is a folded piece of thin viscose, previously sterilised in a glass petri dish. A 1:10 suspension of fine Indian ink is sterilised and employed in the usual manner to make a suspension of spores such that the dots, which are quickly put on the viscose with a sterile nib, each contain approximately one spore. The dots are put *between* the layers of viscose, and the folded piece is then placed under a cover-slip for microscopic examination. Both slide and cover-slip are previously sterilised by flaming, and the cover-slip may be temporarily held down by two drops of immersion oil, as indicated. The position of any dots containing one spore only is noted, the viscose is removed, these dots are quickly cut out (through both thicknesses) with flamed scissors, and each dot is dropped into a little liquid medium. A certain number of the spores so treated will germinate, and thus give rise to authentic single-spore cultures.



This is, of course, merely an adaptation of the older Indian ink methods, but has many advantages that will be obvious to those who have tried such methods.

References

1. R. V. Vernon, *Ann. Bot.*, 1931, **45**, 733.
2. L. D. Galloway, *J. Text. Ind.*, 1935, **26**, 123T.

L. D. Galloway

31, Lake Close
Wimbledon, London, S.W.19

THE DISCOVERY OF VANADIUM INKS

On page 146 of the new edition of Mitchell's "Inks" it is stated that the discovery of the fact that ammonium vanadate forms a black ink with gallotannin is attributed to Berzelius (*Dingler's polyt. J.*, 1835, **56**, 237), but that no reference to the discovery is to be found in the *Jahresberichte* or *Lehrbuch* of Berzelius. Further, it is remarked that the statement that this ink is permanent has been copied from one textbook to another and is still to be found in standard chemical works.

In the years 1834–1841 there appeared in Holland a Dutch translation of Berzelius' Textbook in six volumes. In the preface to this edition it is stated (the translations into English are mine):—". . . Berzelius has kindly assured me that he will send me any material necessary to add to the German translation, which was begun two years ago. Hence, the present translation has the advantage of being a new edition of his Textbook. . . ."

The second volume of this "new edition," which appeared in 1835, contains, on page 347, the following passage:—"When mixed with an infusion of galls the vanadates of ammonium form a black liquid, which may be used as a most excellent writing ink. The quantity of the salt necessary to give the ink its perfect blackness is so small that it need not be taken into consideration, as soon as vanadium has come into more general use. The writing done with this ink is absolutely black. Acids turn it blue without, however, destroying all traces of the ink, as they do when applied to ordinary ink prepared with iron salts. Alkalis, in the degree of dilution in which they do not attack paper, do not dissolve the ink; chlorine destroys the black colour, yet does not delete the writing, even when a stream of water is afterwards applied to it. In a word, although this ink is not entirely indelible, it clearly withstands those reagents which cause the immediate disappearance of writing in ordinary ink; moreover, it is much blacker and much more fluid, for it consists of a solution and not of a precipitate distributed throughout a solution of gum. It remains to be seen how it will keep in the long run."

Again, in the sixth edition of *Gmelin's Handbuch* (Vol. II, Part II) it is stated, on page 259, under the heading Vanadinsaures Ammoniumoxyd:—". . . Die wässrige Lösung giebt mit Galläpfelaufguss eine schwarze Flüssigkeit, die als fast unauslösliche Tinte dienen kann (Berzelius). Doch verblassen die mit dieser Tinte gescriebenen Schriftzüge bei langjährigem Liegen. Berzelius' Briefe sind ganz unleserlich geworden—Wöhler (Privatmittheil.)."

From the foregoing statements I think that the following conclusions may be drawn:—Berzelius discovered vanadium ink in the year 1835 and communicated his discovery to the translator of the Dutch edition of his Textbook and to the Editor of *Dingler's Journal*. He wrote several letters in the ink to Wöhler, who informed him in due course of the fugitive character of the ink. Hence the description of the discovery may have been withdrawn from subsequent editions of the Textbook. It would be of interest to find out whether the Dutch translation is the only place in which the discovery is given in Berzelius' own words.

J. Zernike

Dommelhoefstraat 1c
Eindhoven, Holland

THE BRITISH PHARMACOPOEIA TEST FOR MEDICINAL PARAFFIN

The Addendum to the British Pharmacopoeia, which became official in January, 1937, describes the sulphuric acid colour test for liquid paraffin, but the standard colour glasses are given in terms of the measurement adopted at the National Physical Laboratory, Teddington, which are not readily transferable to the Lovibond scale. The limit specified in the test corresponds with a combination of Lovibond glasses, 2·5 red, and 6·5 yellow.

The Tintometer Limited

The Colour Laboratory
Milford, Salisbury

Official Appointments

THE Minister of Health has approved the following appointments:

HUGH AMPHLETT WILLIAMS as a Public Analyst for the Metropolitan Borough of Shoreditch in place of H. G. Harrison (retired) (March 8th, 1937).

JOHN EZRA WOODHEAD as a Public Analyst for the Metropolitan Borough of Lambeth, in addition to A. H. M. Muter (April 17th, 1937).

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

CHEESE "DE LUXE"

ON April 13th a wholesale firm was summoned by the Durham County Council at Castle Eden for giving a false warranty with respect to cheese described as "cheese de luxe," which, the prosecution contended, meant cheese of first quality, whilst the defence submitted that the words had no meaning in the trade.

Mr. C. J. H. Stock, B.Sc., F.I.C., County Analyst for Durham, said that he had analysed the cheese and was of opinion that it must have been made with partially skimmed milk. The percentage of fat in the dry matter in the sample was 34·6, whilst in cheese made from full-cream milk the percentage of fat in the dry matter was not less than 45. The price of the cheese was 3d. for a small box, which worked out at 1s. 8d. per lb. In his opinion this was a cheese of inferior quality, and the words "de luxe" were a misdescription. Mr. E. Hinks, B.Sc., F.I.C., Public Analyst for Surrey, gave evidence in support of the prosecution.

Mr. Fenwick, for the defence, submitted that the words had no meaning in the trade, and, in support of his contention, produced a number of articles of tinned goods and other articles marked "de luxe." He asked that the case should be dismissed on its merits.

Dr. J. T. Dunn, F.I.C., Public Analyst for Northumberland, said that, as a half-milk cheese sold at 3d. per packet, the cheese in question was quite a good cheese of its kind.

Representatives of firms of provision merchants and grocers gave evidence to the effect that the words "de luxe" had no commercial meaning, and that neither the retailer nor the consumer would be misled by them.

Dismissing the case, the Chairman of the Bench remarked that although it was deplorable that such words should be used, undoubtedly they were used, and nobody attached any definite meaning to them. On the application of Mr. Fenwick, £5 5s. costs were allowed to the defendants.

FULL-FRUIT STANDARD BLACKCURRANT JAM

FALSE WARRANTIES

ON April 20th, 1937, a firm of jam manufacturers was summoned at Kensington Petty Sessions by the Kensington Borough Council for giving false warranties to retailers in respect of two samples of full-fruit standard blackcurrant jam.

The summons against each retailer of these jams, with regard to the samples not being of the quality demanded, had been dismissed at a previous hearing, both defendants pleading a warranty.

Mr. Glyn Jones prosecuted for the Borough Council, and Mr. Christmas Humphreys defended.

Mr. Glyn Jones, opening the case, said that the proceedings were taken under Section 30 of the Food and Drugs (Adulteration) Act. The Public Analyst for the Royal Borough of Kensington, Mr. F. W. Edwards, F.I.C., reported that sample No. 1 contained not more than 18 per cent. of blackcurrants, and sample No. 2 not more than 13 per cent.

It was pointed out that the defendants had agreed to adopt the standards of the Food Manufacturers' Federation; notwithstanding this fact, the jams were not only of very inferior quality, but even the labels used showed grave departures from the correct method of labelling laid down by the Federation. For instance, sample No. 1 had the additional words "and other fruit juice" and "improved with the addition of fruit juice," and sample No. 2 made no reference to the standard of the Food Manufacturers' Federation, and also had the additional words "with other fruit juice."

Mr. Glyn Jones said that the remainders of the two samples analysed by Mr. Edwards were submitted to a joint analysis by Mr. Thomas Macara, F.I.C., Director of Research for the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery, and Jam Trades, and also of the British Food Manufacturers' Research Association, and Mr. Edward Hinks, B.Sc., F.I.C., Public Analyst for the County of Surrey. Their results were in substantial agreement with those of Mr. Edwards. Counsel further remarked that the defendant Company applied at the previous hearing for the reserved portions of the two samples to be sent to the Government Chemist for analysis. The Government Chemist had now completed his analyses, and his certificates showed results in close agreement with those of Mr. Edwards and the others. In respect of No. 1 the Government Chemist certified that, having regard to the natural variations in the composition of blackcurrant fruit, he was of opinion that the sample might have been prepared with as little as 10 per cent., or as much as 18 per cent., of blackcurrants; similarly, in respect of No. 2, that the jam might have been prepared with as little as 7 per cent., or as much as 13 per cent., of blackcurrants.

Counsel said that, in addition to Mr. Edwards, the two other expert witnesses who actually analysed the remainder of both samples would be called, and their evidence should leave no doubt in the minds of the Bench about the quality of these jams.

Mr. F. W. Edwards, F.I.C., the Borough Analyst, said that he obtained the following results on analysis of the two samples:

	No. 1	No. 2
Fruit-content (per cent.) on average insolubles	15	11
,, ,, ,, ,, ,, minimum ,,	18	13
,, ,, ,, ,, ,, average acidity	21·4	19·6
,, ,, ,, ,, ,, minimum ,,	25·7	23·5

He said that in calculating the fruit-content from the insoluble solids he had reported figures based on the *minimum* insoluble solids found in blackcurrants, thus giving the maximum benefit to the defendants. Likewise, in using the acidity figures, he had credited to the blackcurrants the acidity due to the added fruit juice, and yet the jams were well below the standard.

Asked by Mr. Humphreys to explain the results of the analyst for the defence, who obtained a minimum percentage of fruit 21·6 per cent., and a maximum 36·4 per cent., on one of the samples, Mr. Edwards said that, in view of such close agreement between his own results and those of the Government Chemist, Mr. Hinks and Mr. Macara, it was not for him to justify the defendants' analyst's results; rather it was for that gentleman to explain the discrepancy between his results and those of all the others. Mr. Edwards further pointed out that even if the insoluble solids were not evenly distributed, the acidity would remain practically constant. He said that in his experience the standards of the Food Manufacturers' Federation were loyally observed by makers of jam, the samples constituting this particular batch being the first, among some hundreds he had examined, that had failed to reach them.

Before Mr. Macara and Mr. Hinks could be called to give evidence for the prosecution, Mr. Humphreys said that in view of the evidence he had heard, he would like to address a few words to the Bench to simplify matters and save time. The defendant Company's analyst had not determined the acidity, and they were therefore obliged to admit that the prosecution had proved their case in so far as the deficiency in fruit-content was concerned, but he would call evidence to show that the defendants had reason to believe, when the warranties were given, that the jams were in fact of full-fruit standard.

The manager and the foreman of the company's Croydon branch gave evidence that the jams were manufactured from imported sulphited blackcurrant pulp received in barrels, and compounded according to a formula supplied to them by their head office, but they both admitted in cross-examination that they had no chemical knowledge, and that there was no works chemist to check the quality of the raw materials or to examine the final product. The formula on which they worked should have produced a blackcurrant jam containing 31·5 per cent. of the named fruit.

In his concluding speech Mr. Humphreys said that his clients were a large company doing a substantial trade, and for a number of years there had been no complaint about their products. It was true, he had to admit, that there was some serious mistake which his clients would seek to rectify in their own interests, but he asked the Bench to believe that they had acted in good faith. In view of their clean record he submitted that the summons be dismissed on payment of reasonable costs.

After deliberation, the Bench dismissed the summons under the Probation of Offenders Act on payment of fifty guineas costs.

The National Physical Laboratory

REPORT FOR THE YEAR 1936*

THE Lord President of the Council, after consultation with the Council of the Royal Society, appointed Sir Frank Smith, K.C.B., C.B.E., F.R.S., Secretary of the Department of Scientific and Industrial Research, to hold the office of Director pending the appointment of a successor to Sir Joseph Petavel. The Executive Committee pay a tribute to the memory of Sir Joseph Petavel, who had held the post since 1919.

SCIENTIFIC ASSISTANCE TO INDUSTRY.—Firms experiencing difficulties of a technical nature are invited to communicate with the Director, who will advise them whether the Laboratory is in a position to afford assistance on any particular question. While the experimental work required in researches and investigations for industry is normally carried out at the Laboratory, the Committee will be prepared, in appropriate cases, to send members of the staff to manufacturers' works to survey the problem and, where appropriate, to carry out the investigation under the conditions obtaining in industry. It is hoped that this extension of the facilities offered by the Laboratory will prove of considerable assistance.

The work of the Laboratory includes the design and construction of instruments for carrying out the tests undertaken, and in many cases the Committee are prepared

* H.M. Stationery Office, Kingsway, London, W.C.2. Price 2s. 6d. net.

to place the designs of such instruments at the disposal of firms desiring to construct them.

Lectures have been given in provincial centres on various aspects of the work of the Laboratory by members of the staff, and during the year the Laboratory has taken part in several technical exhibitions.

The Report surveys only a few of the varied researches completed or in progress in the several departments of the Laboratory.

STANDARDS.—A noteworthy example of work on precise standards is a redetermination of the value of the International Ohm in absolute units, completed during the year. Two methods are in use at the Laboratory for making this measurement, namely, the Lorenz and the Campbell methods. The result of this work has been to show that the International Ohm is equal to 1·00050 ohm in absolute units, and further that the results of the two methods are in agreement to within 1 part in 100,000, that is to within less than the maximum probable error of either. This work is of considerable importance, for the question of electrical units will come before the International Committee of Weights and Measures next year in connection with the decision to adopt, in 1940, in place of the present system of International Units, new units based on absolute measurements.

THE RÖNTGEN.—Another example of the establishment of precise standards is the work on the units of X-ray and gamma ray intensity. During the past year X-ray and radium dosage have been correlated in terms of a common unit (the röntgen)—a matter of fundamental importance to the medical profession.

MEASUREMENT OF RADIUM.—Since the Laboratory began this work 130 g. of radium (one-fifth of the world's estimated supply) have been tested. The amount of radium in Great Britain is believed to be of the order of 100 g., about one-quarter of which is at present owned by the National Radium Trust, for which body, and for the Radium Commission, the Laboratory has continued to conduct the more technical aspects of their work.

RATIO OF SPECIFIC HEAT OF GASES AT HIGH TEMPERATURES.—Measurements up to 1800° C. of the ratio of the specific heats of carbon monoxide by the velocity of sound method have given results agreeing well with values calculated from spectroscopic data. More recently, observations on carbon dioxide and argon up to 1000° C. have been completed.

THERMAL CONDUCTIVITY.—An apparatus has recently been designed for measurements of the thermal conductivity of gases up to high temperatures; it is of the concentric tube type, employing radial heat flow from a hot wire across a narrow annulus of gas. So far the apparatus has been successfully used with air and carbon dioxide up to 300° C.

Calcium Chloride Brines.—A concentric tube method has been used for measuring the thermal conductivity of calcium chloride brines of various concentrations, a heater being placed within the inner tube, whilst the outer tube was maintained at a lower temperature. The results, which are of service in refrigeration, show that the thermal conductivity decreases regularly with increasing density, the value for brine of density 1·38 g. per ml. being 20 per cent. less than that for pure water.

Metallic Conductors.—The thermal conductivities of some 20 alloy steels are being measured at temperatures up to about 800° C. in a type of longitudinal heat-flow apparatus. The thermal activity of specimens of Acheson graphite has also been measured in the same type of apparatus. The conductivity falls rapidly with rise in temperature; that of one specimen decreased from 0·4 cal. per cm.^{2} per second at 0° C. to about 0·16 at 800° C.

VISCOSITY OF BRINES.—The viscosities of calcium chloride brines of densities up to 1·39 g. per ml. have been measured at temperatures down to $-15°$ C., in an apparatus of the falling plug type, modified from that previously described for measuring the viscosities of refrigerants. The viscosities varied about fourfold in the range −15° C. to +35° C., the strongest brine having a viscosity about four times that of water at temperatures from 0° C. to 35° C.

INTERNATIONAL TEMPERATURE SCALE.—Much attention has been devoted to that part of the International Temperature Scale, from 660° C. to 1063° C., which is realised in practice by the standard platinum, 10 per cent. rhodium-platinum thermocouple. Several improvements have been made which will increase the accuracy of reproduction from ±0·1° C. to ±0·02° C.

THE CHECKING OF THERMOCOUPLES.—For checking thermocouples at the sulphur boiling-point (444·6° C.) a new form of apparatus has been constructed, in which a single envelope of "Pyrex" glass contains the receptacle of the sulphur, a closed re-entrant tube for insertion of the thermocouple and an open projecting tube to serve as condenser. The heating element is a platinum wire, mounted on a refractory tube and with its ends sealed through the envelope, the whole being immersed in the liquid sulphur. The apparatus is very convenient in operation and avoids the risk of cracking the envelope on remelting the sulphur, which is liable to occur with the usual type of apparatus depending on the external application of heat.

DIELECTRIC PROPERTIES OF DRY-CLEANING REAGENTS.—Measurements of dielectric properties have found another application in connection with the reagents used in the dry-cleaning industry. Most of the liquids used in this industry are very good electrical insulators. Thus charges developed by friction or otherwise in the course of the cleaning process are not always able to leak away, and it is possible for accumulated charges to cause a spark, which may lead to an explosion. It is usual to add various soaps to the cleaning liquid, and, at the request of the Home Office, experiments have been made to ascertain what effect this practice has on the risk of explosion. The conductivities of a typical liquid with and without the addition of various soaps were measured by the methods developed for the testing of insulating oils. It has been established that the addition of the soaps always causes a considerable increase of electrical conductivity, and it is inferred that the risk of explosion is thereby lessened. During the process of cleaning, however, the conductivity of the liquid falls: the fabric evidently destroys the action of the soap, probably by absorbing one of its constituents. Further experiments are in progress.

MAINTENANCE OF PHOTOMETRIC STANDARDS.—The Laboratory is joining with the National Bureau of Standards, the Laboratoire Central d'Electricité and the Physikalisch-Technische Reichsanstalt in proposing to the International Committee of Weights and Measures (through its Advisory Committee on Photometry) that the unit of candle-power be changed slightly at the colour temperature of carbon filament lamps, so that the brightness of a black body at the temperature of solidification of platinum becomes 60 new units instead of approximately 59 international candles. This proposal has an important practical advantage in that it leaves almost unchanged the unit of candle-power at present in current use for lamps operating at the colour temperature of tungsten filament vacuum lamps, and considerably reduces the change necessitated in the present unit for gas-filled lamps. Changes in these units are necessitated by the fact that the now internationally agreed photometric procedure for bridging a difference of colour temperature gives results which are not exactly in agreement with the results obtained by following the various procedures hitherto adopted at the national laboratories.

PHYSICAL PHOTOMETRY.—The main problem underlying the employment of physical photometers for photometric purposes is that of obtaining the desired colour response. For general use the photometer must possess a colour sensitivity curve very closely conforming to that internationally adopted as representing the average eye.

Assuming that a photoelectric cell and a colour-correction filter are under consideration, the necessary data for the solution of the problem are the spectral transmission values of materials or of chemical solutions suitable for the colour filter in various thicknesses or concentrations, and the corresponding relative sensitivity values for the photo-cell throughout the spectrum.

To facilitate the large amount of spectrophotometric work involved, a photo-electric spectrophotometer has been designed and built which very materially shortens the time required for measurements, as compared with visual methods, with no loss of accuracy. The optical system of the instrument centres in a Hilger Tutton constant-deviation monochromator. The photo-cell used is a modern type of cell of the potassium-on-silver-oxide thin-film type, and the electrical circuit is the standard type of thermionic valve bridge with high-slope general service valves. A description of the instrument has been published (Preston and Cuckow, *Proc. Phys. Soc. London,* **1936, 48,** 869).

METALLURGICAL APPARATUS AND METHODS.—*Use of Flame Spectra.*—Some work has been done on the use of flame spectra, the solution being sprayed into a Bunsen burner supplied with acetylene. Although the luminosity is low, it has been found possible to obtain estimates of the proportion of some alkali metals present in small concentration in a mixture. The method has the advantage of not requiring the preparation of standard alloys, as for the arc and spark spectra methods.

Oxygen in Steel.—The apparatus for determining the total oxygen by the vacuum fusion method has been so far improved that the results can be accepted with confidence. To reach such a condition, a study had to be made of the behaviour of graphite powder as an electrical and thermal insulator in a high-frequency electric field. It is now practicable to remove the gases from the apparatus at 2200° C., instead of at 2000° C., thus reducing the time of removal from 4 hours to 2 to 2½ hours, and the blank correction has been lowered from 0·07 ml. to 0·02 ml. of gas in an hour. As a determination at the usual temperature of 1550° C. lasts only 15 minutes, the correction is negligible.

Oxides in Steel.—As a means of isolating the oxides in steel and making an analysis of them, the alcoholic iodine method has been used, and further improvements in the stirring apparatus have been made in order to shorten the time taken for solution. By controlling the temperature, the results are made very consistent, and the method can now be used with confidence for the simpler steels. The difficulty of high sulphur content is being overcome, and work is in progress on the study of steels containing carbide-forming elements, such as chromium.

Milk and Nutrition

NEW EXPERIMENTS REPORTED TO THE MILK NUTRITION COMMITTEE*

AN informal conference called by the Milk Marketing Board's Advisory Committee on Milk Publicity, and consisting of representatives of Government Departments, the Medical Research Council, the Milk Marketing Boards and other interested bodies met towards the end of 1934 to consider what further investigations were required on the nutritive value of milk, and from this conference a special committee—the Milk Nutrition Committee—was formed to undertake the task of conducting these investigations, the necessary funds for which were to be provided out of grants from the Exchequer under the Milk Act of 1934 and from the English and Scottish Milk Marketing Boards.

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* Part I. The Effect of Commercial Pasteurisation on the Nutritive Value of Milk, as determined by Laboratory Experiment. From the National Institute for Research in Dairying (University of Reading) and the Rowett Research Institute, Bucksburn, Aberdeen. Pp. 67. 24 Tables. To be purchased directly from the National Institute for Research in Dairying, Shinfield, Reading. 1937. Price 2s. 6d. net. By post 3s.

This Committee first met in December, 1934, under the chairmanship of Lord Astor, to consider the broad outlines of the proposed investigations, and a sub-committee was appointed to draw up a detailed scheme of research.*

Among the investigations finally agreed were experiments planned to decide as precisely and unequivocally as possible what was the effect of pasteurisation on the nutritive value of milk. It was considered that properly designed experiments, where almost every factor could be adequately controlled, offered excellent prospects of clear-cut results, and the National Institute for Dairying Research and the Rowett Institute were asked to undertake this work.

The present Report deals with the results of the work with rats and that on the direct chemical estimations of vitamin potency.

Measures were taken to ensure reasonable uniformity of technique in the two laboratories, and the following investigations were planned, rats to be used in all the experiments except 3(*a*) and 3(*c*), in which direct chemical or physical methods were to be employed.

1. The effect of commercial pasteurisation on the nutritional availability of calcium and phosphorus of milk.
2. The effect of commercial pasteurisation on the biological value of milk proteins.
3. The effect of commercial pasteurisation of milk on the following constituents:
   (*a*) Vitamin *A* and carotene;
   (*b*) Vitamin *B* complex;
   (*c*) Vitamin *C*.
4. The effect of commercial pasteurisation on the total nutritive value of milk.

The general conclusions drawn from the results, which are given in detail, are as follows:

The results show that the nutritional availability of the calcium and phosphorus in the milk is unaffected by pasteurisation. Whatever small changes in the state of combination or colloidal condition of these two constituents have been found by experiments *in vitro* appear, therefore, to be without nutritional significance. The results also prove that the biological value and true digestibility of the nitrogen are not affected by the holder process. When used for rats as an exclusive diet, pasteurised milk supplemented with iron, copper and manganese is not inferior to raw milk supplemented in the same way. (In both cases these mineral supplements are necessary in order to avoid nutritional anaemia, which would otherwise overshadow the point at issue.)

So far as vitamins are concerned, neither the vitamin *A* itself nor the provitamin, carotene, is affected by heat treatment; on the other hand, vitamin *B* (undifferentiated) suffers some loss, very probably (but not certainly) mainly in the more heat-labile B_1 fraction. Heat treatment also causes a loss of some of the vitamin *C* originally present in the milk, the loss in these experiments being some 20 per cent. of the original vitamin *C* content of the milk. Commercial pasteurisation *per se* is not, however, alone to blame for this loss. Experiments, reported elsewhere, carried out in the Nutritional Laboratory of the National Institute for Research in Dairying have shown that milk which has never been exposed to light can withstand holder pasteurisation without any loss of ascorbic acid. It is the more labile form of this vitamin, reversibly oxidised under the action of light, which is destroyed by this process; reduced ascorbic acid itself, the form in which the vitamin is secreted by the normal cow, is not affected.

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* This Expert Sub-Committee consisted of the following:—Sir John Boyd Orr, D.S.O., M.D., F.R.S. (*Chairman*), Sir William Dampier, Sc.D., F.R.S., J. Alison Glover, O.B.E., M.D., F.R.C.P., Professor H. D. Kay, O.B.E., D.Sc., F.E. Knight, F. Mander, M.A., B.Sc., Professor E. Mellanby, M.D., F.R.C.P., F.R.S., P. L. McKinlay, M.D., Professor D. M. S. Watson, D.Sc., F.R.S., and H. E. Magee, M.B., D.Sc. (*Secretary*).

The extent to which findings obtained with the rat as experimental animal are capable of application to the problems of human nutrition, and more particularly the bearing that the results recorded in this Report may have on the question of the advisability or otherwise of pasteurising milk for human consumption is not discussed. It is intended to deal with these points in due course, but to wait until the findings of the investigations on calves and school children (which are in progress) become available, so as to have a wide basis of assessment.

Of special interest to analysts are the results reported in the main series of experiments, "designed to detect the effects (if any) of pasteurisation on the availability of the calcium and phosphorus of milk." For this purpose the precise intake of calcium and phosphorus in the animals' food was carefully measured, by "weighing back" all unconsumed food, allowing for its loss in moisture from the time of offering, and determining by analysis the calcium and phosphorus actually consumed. Moreover, the technical difficulties were further increased by working on the "paired feeding" system, that is, reducing the food intake of each pair to that of the less avid of the pair. Furthermore, precise determinations of calcium and phosphorus had also to be made in the urine and faeces of the experimental animals, and finally in the whole carcases of the animals after they had been killed at the end of the experiment. In order to determine the amounts of calcium and phosphorus that had been deposited by the animals during the experimental period, one further series of data was required, namely, the amount of calcium and phosphorus in the animals' bodies at the beginning of the experiment. This could, of course, only be obtained indirectly, and was so obtained by analysing for calcium and phosphorus the carcases of the animals' litter mates at the beginning of the experimental period.

This arduous investigation led to gratifying conclusive results. The difference between the amount absorbed (itself the difference between the amount eaten and the amount excreted) and the amount deposited was in no animal more than 2·0 per cent. for phosphorus and 0·2 per cent. for calcium. The authors believe that the somewhat greater discrepancy with phosphorus is almost certainly due to slight loss of phosphorus during the ashing of the carcases of the large animals at the end of the experimental period. The agreement for calcium is astonishingly good.

Although the results of these experiments fail to show, at the levels fed, any significant difference between the utilisation of calcium and phosphorus from raw and pasteurised milk, except a slightly significant difference in favour of pasteurised milk for the calcium retention of does, the experiments were well worth carrying out, partly because they seem to have settled in a clear manner what was a much vexed problem, but equally because they constitute a model of analytical procedure for such work. A. L. B.

Department of Scientific and Industrial Research. New Zealand

TRACE ELEMENTS IN RELATION TO BUSH SICKNESS*

The investigation described was carried out to compare the effects of feeding iron compounds and some trace elements to bush-sick sheep.

The results show that iron and ammonium citrate made from specially pure reagents was not satisfactory. This is further supported by the fact that one of the iron-and-ammonium-citrate-treated ewes when transferred to cobalt improved immediately. Reakes and Aston (*N.Z. J. Agric.*, 1919, **18**, 193) obtained good results on treating cattle with iron and ammonium citrate (Howard and Son's Fer. et Ammon. Cit. P.B.), but a present-day sample of this make contained 7 p.p.m. of cobalt. They found other iron salts, such as ferrous lactate, less efficient, but comparable samples were not obtainable for analysis.

The Australian limonite is very high in cobalt, a daily dose containing 1·54 mg. of total cobalt, or 0·233 mg. extractable with $N/10$ hydrochloric acid. A Ruatangata (Reyburn) limonite dose contained 0·24 mg. total cobalt, or 0·016 mg. extractable with $N/10$ hydrochloric acid. Only one trial was made with Australian limonite. A ewe stated to be definitely bush-sick at the beginning of the experiment was, after treatment with Australian limonite, reported to be no longer bush-sick.

Kenya iron oxide cured a semi-sick hogget at Kaharoa, but has been unsuccessful at Atiamuri. The total cobalt-content was high, giving 0·21 mg. per dose. This substance is highly alkaline (11 per cent. of alkalinity expressed as sodium carbonate), and the amount of soluble iron in a $N/10$ hydrochloric acid extract of it was very low. The cobalt extractable with $N/10$ hydrochloric acid in the daily dose was a third of that in Reyburn limonite. "Lux" (iron oxide) was also high in cobalt, a daily dose containing a total of 0·17 mg., or 0·019 mg. extractable with $N/10$ hydrochloric acid. This compound was also alkaline, but was well washed before using. It was not satisfactory at Atiamuri, and, when the treatment was changed to cobalt, a quick recovery was made. It is suspected that some substance harmful to the animal may be present in the "Lux." Owing to lack of material, only one sheep could be treated with "Lux," and the results are therefore inconclusive.

Reyburn limonite was consistently effective, yet the iron-free extract of this limonite gave a negative result at Atiamuri with the one sheep under trial. The cobalt-content per dose was 0·06 mg., a quarter of the total cobalt in the Reyburn limonite. It would appear that traces of catalytic elements other than copper and cobalt, and possibly including nickel, manganese, and zinc, may be necessary to effect the complete utilisation of iron in soils and pastures. There appears to be no deficiency of copper. Underwood and Filmer (*Austral. Vet. J.*, 1935, **11**, 84) refer to the curative effects of cobalt demonstrated by Marston (1935) and Lines (1935) in preventing and curing "coast disease" in South Australia, and have shown that it has similar results with enzootic marasmus in Western Australia. Good results were obtained here by feeding 1 mg. of cobalt alone per day to bush-sick sheep. It is possible that when no available iron is added to the diet a larger amount of cobalt is required to make the iron present in the soils and pastures available for animal nutrition.

* By Eunice M. Wall. Chemistry Section, Dept. of Agriculture, Wellington. 1937. Government Printer, Wellington, N.Z.

COBALT-CONTENT OF LIMONITES USED IN THE TREATMENT OF BUSH SICKNESS*

A PRELIMINARY examination of the cobalt-content of some New Zealand limonites (Grimmett and Shorland, *N.Z. J. Agric.*, 1935, **50**, 367) showed that an effective Ruatangata limonite contained approximately 3 p.p.m. of cobalt extractable with *N*/10 hydrochloric acid, whereas the ineffective Puhipuhi and Onekaka ores showed only faint traces of cobalt in extracts from 200 g. of the sample (unpublished results).

At this point it was evident that a more sensitive method for the micro-determination of cobalt was necessary, and accordingly a sensitive modification of Stare and Elvejem's method (*J. Biol. Chem.*, 1932–3, **99**, 473) has been devised. In order to obtain an indication of the amount of cobalt likely to be absorbed during digestion by sheep and cattle the limonites were treated as follows:—One hundred g. of the sample were shaken for 24 hours with 2 litres of hydrochloric acid of *N*/10 strength after neutralisation of any alkalinity in the sample. The ratio of the weight of limonite to the volume of *N*/10 acid must be kept constant if the results are to be comparable. After filtration the silica was removed, and the filtrate with a few drops of hydrogen peroxide (to ensure that all iron will be in the ferric state) was evaporated until the acid reached constant boiling-point strength and the excess of peroxide was destroyed. Iron was then removed as chloride by continuous extraction with ether in the apparatus shown in Fig. 1.

The ether-extracted solution was evaporated to 50 ml. and an aliquot portion was taken for the determination of cobalt. To destroy any organic matter the solution was evaporated to dryness, and a little sulphuric acid was added to remove chlorides; the residue was ashed at about 500° C., and then taken up with hydrochloric acid of constant b.p., and the cobalt was completely extracted from any residual calcium sulphate.

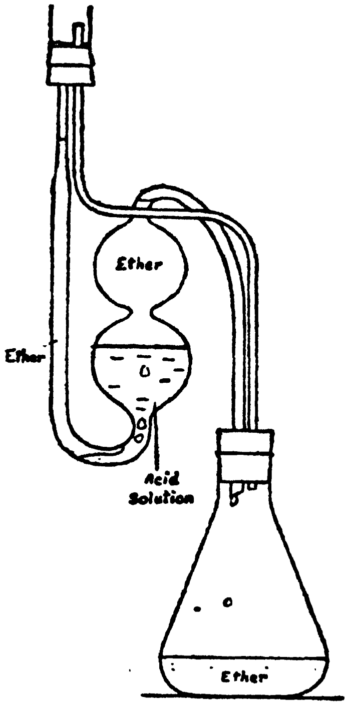

Fig. 1

The cobalt was determined as follows:—From 5 to 10 ml. of the solution were heated to about 70° C. with 2 g. of hydrated sodium acetate and a few drops of phenolphthalein solution as indicator, then first made just alkaline with potassium hydroxide and afterwards brought to about *p*H 8 with weak hydrochloric acid. A small excess of nitroso-R-salt reagent (Van Klooster, *J. Amer. Chem. Soc.*, 1921, **43**, 746) was added (0·4 ml. of a 0·5 per cent. solution is a convenient amount for the determination of 0·02 mg. of cobalt), the solution was boiled for about a minute, and then treated, drop by drop, and with constant stirring, with 2 ml. of conc. redistilled nitric acid added at the rate of about 1 drop per second. After about 30 minutes the solution was made up to 20 ml. and the resulting colour was matched with those of a series of standards in Nessler tubes.

This method gave accurate results in the presence of nickel, titanium, chromium and vanadium, but copper, ammonium salts, ferrous salts, cyanides, persulphates and peroxides interfered. As much as 30 per cent. of the cobalt present was occluded in the hydroxides precipitated from 1 g. of Ruatangata limonite, but losses by the ether extraction method were negligible.

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* By K. J. McNaught, Chemistry Section, Dept. of Agriculture, Wellington. 1937. Government Printer, Wellington, N.Z.

The iron oxide residue from bauxite works, which is believed to be similar to that found to cure Nakuruites in Kenya, contains a considerable amount of cobalt (91 p.p.m. total, and 2·0 p.p.m. soluble in *N*/10 HCl), and the Australian limonite used by Filmer (*Australian Vet. J.*, **1933**, **9**, 163) in the treatment of enzootic marasmus in Western Australia is very high in cobalt (363 p.p.m. total, and 55 p.p.m. soluble in *N*/10 HCl). It contains, however, about 0·2 per cent. of chromium, which may affect its value. Howard and Son's ferric ammonium citrate contained 7 p.p.m. of cobalt. Prior to the introduction of the very efficient Ruatangata limonite, ferric ammonium citrate was widely used to combat bush sickness, frequently with excellent results, and its value may possibly have been due to the presence of cobalt in association with the iron.

The tabulated results indicate that the effectiveness of the limonites examined for the treatment of bush sickness runs roughly parallel with their cobalt-content, although one Okaihau sample, with total cobalt 14 p.p.m., is anomalous. Field reports concerning the more recently marketed Okaihau limonite have been mainly favourable, although in a few instances unsatisfactory results have been reported. The total cobalt in 15 samples ranged from 281 to 5·2 p.p.m. on the dry substance, and the cobalt in *N*/10 hydrochloric acid extract in 8 of these samples from 8 to 1 p.p.m. If cobalt is the factor determining the efficacy of these limonites, there is an immediate explanation of the rather conflicting results with Okaihau limonite. Samples collected from the eight deposits at Okaihau show an astonishing variation between 12 and 281 p.p.m., although the amounts extractable with *N*/10 hydrochloric acid show a much smaller variation.

The bush-sick soils of the Rotorua district average 0·12 p.p.m. of cobalt extractable by *N*/10 hydrochloric acid, whereas the healthy soils average 0·61. It is significant that the soil from a healthy change paddock at Hamurana in the bush-sick area contains as much cobalt as an average healthy soil. Soils from Morton Mains, Southland, are intermediate, but from the few results available the cobalt-content appears to be no guide as to the incidence of the "Morton Mains disease." (See also ANALYST, 1935, **60**, 87; 1936, **61**, 38.)

Government of India

REPORT ON THE CHEMICAL LABORATORIES, CENTRAL BOARD OF REVENUE, 1935–36

THE Control Laboratory, under the direction of Dr. H. B. Dunnicliff, F.I.C., is located in the Government College, Lahore, and there are also Custom House Laboratories at Bombay, Calcutta, Karachi, Madras, and Rangoon, and an opium factory at Ghazipur.

The total number of Customs samples examined in the various laboratories was 33,886, an increase of 450 over the previous year.

GLYCOLS IN FLAVOURING ESSENCES.—The use of glycols in place of ethyl alcohol as solvents for flavouring essences is increasing. In distillation it was noticed in several instances that, owing to some of the glycol being carried over by the steam, the specific gravity of the distillates exceeded 1·000.

ESSENTIAL OILS.—The standard methods approved by the Essential Oil Sub-Committee of the Analytical Methods Committee, published in THE ANALYST, were used in testing the 142 samples of essential oils examined.

TEXTILES AND YARNS.—Of the 1194 samples examined, 941 involved quantitative analysis. Attempts have been made at Bombay to standardise the estimation of artificial silk in textiles by boiling with dilute hydrochloric acid, rubbing the mass to a powder, and extraction with water.

At Karachi the determination of the composition of fabrics containing several constituents by an optical counting method, on the principle of the Spence and Krauss method of estimating mechanical wood pulp in paper, is giving satisfactory results.

PAPER.—A number of appeals against port decisions have been referred to the Central Laboratory for analysis both by the fibre-count and volumetric methods. The close agreement with the results obtained at port laboratories by the much-discussed Spence and Krauss method is remarkable in view of the doubt thrown upon the optical method of estimating mechanical wood pulp in paper.

At Bombay an investigation is being made into the efficiency of the estimation of mechanical wood pulp in paper by Halse's lignin method.

CUSTOMS RULING ON MANURES.—The Customs Ruling No. 2 of 1932, which required manures to be imported in the form and degree of impurity which is characteristic of the chemicals in question when intended for manure, has been amended by Ruling No. 2 of 1936, dated April 18th, 1936, which omits the words "and degree of impurity."

DISCOLORATION OF OPIUM.—Progress has been made in the investigation of the causes of the discoloration of morphine hydrochloride during storage. Difficulties have been experienced in the isolation of the degenerated product. A dark coloured substance separated when a 10 per cent. w/v solution of morphine hydrochloride stored in an ordinary plain white glass bottle was exposed to light for three years.

In an article entitled "Loss of Morphine in Indian Opium on Storage," by Dunnicliff, Rây and Singh, published in the *Journal of the Institute of Natural Sciences, Calcutta*, 1935, **1**, 107, a misunderstanding has been caused by the use of the word "storage." In the opium factory this means the storage, in open vats, of large quantities of general opium just as it is received at the factory. In this condition it is subject to atmospheric oxidation, and a marked loss of morphine occurs during the first six months. Further loss is prevented, presumably, by the exhaustion of the oxygen held mechanically or in solution in the opium and surface protection by the formation of a hard crust on top. In the article "storage" means keeping the opium in closed air-tight containers.

Ceylon

REPORT OF THE ACTING GOVERNMENT ANALYST FOR THE YEAR 1936

THE Acting Government Analyst (Mr. H. Atkinson) reports that the work of the Department is steadily increasing, the number of articles examined being 3544 as compared with 3256 in 1935. Criminal investigation is responsible for a large proportion of the articles, the number of exhibits being 2511 in 937 cases, as against 2015 exhibits in 815 cases in 1936. An Assistant Analyst has been appointed for document work.

POISONING CASES.—In 46 of the 95 cases investigated poison was found, including arsenic in 6, acetic and formic acids in 8, copper salts in 7, metallic mercury in 4, prussic acid in 6, quinine in 2, and strychnine and brucine in 1.

Metallic Mercury Poisoning.—In one of the four cases the mercury was sent to the laboratory in small tin-coated boxes, with the result that a mercury tin amalgam was received. In one of the cases mercury had been given to a 16-day-old child. Metallic mercury was found in the faeces, but the child's life was not endangered. In another case mercury was found in dates that had been given to some little girls. Metallic mercury is reputed to have considerable efficacy as a charm.

PROHIBITED DRUGS.—There was a decrease in the number of cases investigated—156 as compared with 201 in 1935. Ganja was identified in 81 exhibits, and opium in 85. Much of the opium examined was heavily adulterated. In one case a black substance submitted for opium consisted of a black resinous substance containing neither morphine nor meconic acid.

MILK.—The number of samples received has again decreased—from 441 to 412, while the percentage of adulterated samples stands at the appallingly high figure of 62. Of the 257 adulterated samples, 132 showed less than 25 per cent. of added water, 104 gave between 25 and 50 per cent., and 21 showed over 50 per cent. The highest adulteration recorded during the year was 72 per cent.

The absence of a Food and Drugs Act under which proceedings could be taken is keenly felt.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Variation of the Butyric Acid Value in Milk-fat. M. Teply. (*Ann. Falsif.*, 1937, **30**, 23–31.)—The butyric acid value of Grossfeld and Kuhl (ANALYST, 1926, **51**, 305, 416) has now been determined over a period of 1 year for 50 samples of authentic butter and also for the butter from two individual cows—one from the beginning of the lactation period for 5 months, and the other for the same period but after lactation had been going on for about 5 months. The butyric acid value for the butter-fat from mixed milk was found to vary between 22 (February) and 15·8 (August), with a mean of 19, but for individual cows the limit was wider—24·2 to 13·4. The duration of storage of the butter did not have much influence on the value. The information obtainable from the butyric acid value is equivalent to that given by the combined Reichert-Meissl and Wauters-Polenske values. Values obtained for butter-fat adulterated with coconut oil or with margarine show that 25 per cent. of coconut oil may be detected with certainty, but that 10 per cent. may possibly escape detection, whilst the R-M value may allow 25 per cent. to escape detection and the W-P value 10 per cent. With margarine 10 per cent. may be detected by the butyric acid value. In forming a judgment it is important to know if the butter is from mixed milk or from the milk of an individual cow. Samples of the former with values above 17·5 are regarded as genuine, those with values between 17·5 and 16 are suspect, and those with values below 16 are regarded as adulterated. These figures are means and need modification according to the season; the values for winter butter are: for pure, for suspect and for adulterated samples, respectively, 18, 16·5 to 18 and below 16·5, and for summer butter 17, 15·5 to 17 and below 15·5. The limits of the butyric acid value for goats' milk (10 samples) were 10·1 and 15·3, mean 12·1. The tables given include in nearly every instance the corresponding R-M and W-P values, so that comparisons can readily be drawn. D. G. H.

Granadilla (Passion Fruit) Seed from Kenya. (*Bull. Imp. Inst.*, **1936, 35,** 22–23.)—The seeds of *Passiflora edulis* are flat, oval, dark greyish-brown, and about 0·2 inch long and 0·15 inch broad; 100 seeds weighed 9·5 g.; they contained 8·5 per cent. of moisture and, on extraction with petroleum spirit, yielded 22·4 per cent. of a pale yellow oil, which became slightly opalescent on standing but did not dry when exposed to air in a thin film for several days. The oil had the following characteristics:—Sp.gr. at 15·5°/15·5° C., 0·9261; n_D^{20}, 1·4761; saponification value, 190·9; iodine value (Wijs, 1 hour), 141·2; acid value, 0·3; unsaponifiable matter, 0·8 per cent. The residual meal was of a light buff colour with a large number of dark specks, due to the shell, and was free from alkaloids and cyanogenetic glucosides. It contained (calculated to a 7 per cent. oil basis) moisture, 10·2; oil, 7·0; carbohydrates (by diff.), 17·9; crude proteins, 11·3; ash, 1·5; and crude fibre 52·1 per cent. Although the oil would be suitable for soap making, and probably, after refining, for edible purposes, the high proportion of fibre in the meal would make the residue unsuitable for cattle cake or even for fertiliser. D. G. H.

New Colour Reaction for Morphine and its Derivatives. J. A. Sanchez. (*J. Pharm. Chim.*, 1937, **25**, 346–351.)—The reagent consists of 0·30 g. of pure vanillin dissolved in 100 ml. of official (French Codex) hydrochloric acid. Eight ml. of this reagent are added to a few mg. of morphine in a completely dry test-tube, which is then heated for a few minutes in a boiling water-bath; a very stable reddish-violet colour is developed. Derivatives of morphine containing a secondary alcoholic group also give the reaction, but it is essential that the alkaloid or its salt should be in the solid form. Dilaudide, dicodide and eucodal, which are ketonic derivatives containing no secondary alcoholic group, do not give the reaction, but, after reduction with zinc and hydrochloric acid to dihydromorphine, dihydrocodeine and dihydroxycodeine respectively, the reddish-violet colour is obtained. For the examination of these compounds 1 or 2 ml. of the sample are dissolved in 5 drops of conc. hydrochloric acid and 2 drops of water, and heated with 8 g. of granulated zinc on the water-bath for at least 2 minutes, and the liquid is decanted into another tube, or the zinc may be removed with platinum wire. On heating the solution with 1 ml. of the freshly-prepared vanillin hydrochloride reagent on the water-bath, the colour soon appears. E. B. D.

Colorimetric Determination of Small Quantities of Morphine. C. G. Van Arkel. (*Pharm. Weekblad*, 1937, **74**, 134–137.)—The reagent (*cf.* R. Hofmann and N. Popovici, *Pharm. Zentr.*, 1935, **346**; *Biochem. Z.*, 1933, **260**, 27; and J. A. Sanchez, ANALYST, 1935, **60**, 419) is prepared by dissolving 14·4 g. of molybdic acid anhydride in 100 ml. of warm *N* sodium hydroxide solution, and adding to it sufficient of a sodium silicate solution to bring the SiO_2-content to 0·7 g. Ten per cent. hydrochloric acid is then added, with vigorous stirring, until the solution becomes green, after which the mixture is diluted to 900 ml. and placed on a boiling water-bath which is subsequently allowed to cool slowly, any precipitated silica being removed after 24 hours by filtration and the volume made up to 1 litre; the composition should then correspond with $SiO_2,12MoO_3,4H_2O$. To 5 ml. of a solution of the sample to be tested (equivalent to 0·2 to 10 mg. of $C_{17}H_{19}NO,H_2O$) in 1 per cent. hydrochloric acid are added in succession 5 ml. more of the 1 per cent. acid, 2 ml. of the reagent, and 5 ml. of 5 per cent. ammonia. The mixture is diluted to 25 ml., and the blue compound formed by reduction of the reagent is matched in a colorimeter or, preferably, in the step-photometer, against that produced in the same way from a standard solution containing 5 mg. of morphine in 5 ml. of the 1 per cent. acid. The author cannot confirm the statement (presumably of Hofmann and Popovici, *loc. cit.*) that the colour develops fully in 5 minutes and is stable for 6 hours. Colorimeter calibration-curves for 0 to 5 mg. of morphine made after various periods of time, show in fact that after 2 hours the colour is about 20 per cent. less intense than after 15 minutes, and that the best results are obtained if the match is made after 15 to 20 minutes. Reducing agents other than morphine must be removed, and for small quantities of morphine the method offers no greater accuracy than that of Goin (*Pharm. Weekblad*, 1935, **73**, 366). Of the associated alkaloids, narcotine, papaverine and narceine produce only a very weak pale blue colour, whilst codeine, thebaine and meconic acid give negative results; with codeine and thebaine the yellow colour of the reagent disappears. J. G.

Mitraversine and other Alkaloids from *Mitragyna* Species. Raymond-Hamet and L. Millat. (*J. Pharm. Chim.*, 1937, **25**, 391–398.)—An alkaloid was isolated from the bark of *Mitragyna diversifolia* Hooker (Jr.) by the following method:—The bark was powdered, moistened with potassium carbonate solution and extracted with benzene. The benzene solution was extracted with dilute formic acid, and the extract was made alkaline with potassium carbonate. The resulting yellowish precipitate was dissolved in ether, the solution was filtered and extracted with dilute formic acid, and the acid extract was made alkaline to litmus with potassium carbonate solution. The precipitate was collected on a Buchner funnel, washed with water and dried in a desiccator under reduced pressure over sulphuric acid; 0·600 g. of the crude alkaloid was obtained. This base, dissolved in the minimum amount of ether, yielded yellow spangles soluble in acetone. After addition of talc and filtration, the acetone solution was evaporated to dryness, and the residue was dissolved in the minimum amount of acetone. Pearly white spangles (0·022 g.), melting at 263·5°–264·5° C., were thus obtained. The ethereal and acetone solutions were evaporated together to dryness, the residue was dissolved in dilute formic acid, and the alkaloid was separated as described above; it was a white powder weighing 0·130 g. The crystallised alkaloid was considered identical with mitraversine obtained by Field (*J. Chem. Soc.*, 1921, **119**, 887) from the leaves of *Mitragyna diversifolia* Haviland, the species examined being "almost certainly" the same. The crystalline alkaloid from *M. diversifolia* was also compared with mitrinermine from *Mitragyna inermis* and from *Mitragyna stipulosa* (*cf.* Raymond-Hamet and Millat, *J. Pharm. Chim.*, 1934, **20**, 577), and with mitraphylline. With the Mandelin reagent both the crystalline alkaloid and mitrinermine yield a reddish-orange colour changing through orange and orange-yellow to yellowish-green; but the m.p. of mitrinermine was 203·8°–204·3° C., and the elementary composition of mitraphylline differed from that of the mitraversine from *M. diversifolia*. The question whether each species of *Mitragyna* contains an individual alkaloid is therefore to be investigated. E. B. D.

Reaction to Distinguish between Anabasine and Nicotine Sulphates. S. A. Katz. (*Z. anal. Chem.*, 1937, **108**, 408.)—Preparations of the sulphates of anabasine and nicotine occur commercially as insecticides in the form of dark syrupy liquids almost identical in appearance, odour and colour. Most of the identification reactions of nicotine do not serve to distinguish it from anabasine. Both alkaloids, on boiling with alkali, yield vapours which turn red litmus blue. Schindelmeiser's reaction (ANALYST, 1900, **25**, 128) is positive with both alkaloids. Silicotungstic acid gives with acid solutions of either alkaloid a white precipitate decomposed by alkali. Sokolow (*Chem. Pharm. Ind.*, 1935, **3**, 162) showed that, with hydrofluosilicic acid, solutions of anabasine in methyl alcohol give a characteristic crystalline precipitate, whilst nicotine solutions remain clear. Roussin's reaction (*Z. anal. Chem.*, 1903, **42**, 232) serves to distinguish the two alkaloids. To an ethereal solution is added an equal volume of an ethereal solution of iodine. With nicotine a turbidity forms which, in a closed test-tube, gradually settles into large ruby-red crystals of the periodide, $C_{10}H_{14}N_2I_2.HI$. Anabasine solutions remain clear. A. O. J.

Composition of the South American Drug, Boldo. M. Bachstez and G. Cavallini. (*Chim. e Ind.*, 1937, **19**, 126–128.)—The pure alkaloid boldine was isolated from the drug prepared from the leaves and stems of *Boldea fragrans* Juss. (*Peumus Boldus* Molina). The alkaloid crystallises from ether in slightly yellow prisms, the surface of which quickly becomes brown through oxidation. It is almost insoluble in water, dissolves readily in ether and benzene when freshly precipitated, but less easily when crystallised, is difficultly soluble in petroleum spirit, and readily soluble in alcohol, chloroform, acetone, ethyl acetate, and ammonia. Sodium bicarbonate precipitates only a little of the base from acid solutions, while sodium carbonate precipitates it but dissolves some of the base. It gives the following reactions:—Conc. sulphuric acid, red colour; conc. sulphuric acid + 0·05 per cent. of ferric sulphate, blue colour; conc. nitric acid, red colour; Marquis' reagent (formaldehyde + sulphuric acid), violet colour; ferric chloride solution (10 per cent.), brown colour; Beckurt's reagent (N/10 potassium permanganate solution), reduction, colour changing from brown to red; Johannson's reagent (1 g. of ammonium vanadate in 100 ml. of conc. sulphuric acid), blue colour; Marmé's reagent (ammonium molybdate in conc. sulphuric acid), blue colour; Mecke's reagent (1 g. of selenic acid in 200 g. of conc. sulphuric acid), green-blue colour; Orlow-Horst reagent (ammonium persulphate in conc. sulphuric acid), dark green to blackish-brown colour; platinum chloride, yellow microcrystalline precipitate, becoming red-brown and amorphous on addition of potassium iodide; gold chloride, yellow-brown microcrystalline precipitate, becoming blood-red on addition of sodium bromide; mercuric chloride, white microcrystalline precipitate; potassium ferrocyanide, grey-green microcrystalline precipitate; potassium ferricyanide, green-brown microcrystalline precipitate; Dragendorff's reagent, dark brown precipitate partly microcrystalline and partly amorphous;

potassium hydroxide, colourless precipitate redissolving in an excess of reagent; picrolonic acid, yellow microcrystalline precipitate; Reinecke's salt, green-blue crystalline precipitate; flavianic acid, macrocrystalline precipitate, redissolving on heating.

Small quantities of boldine in medicinal preparations give a characteristic milky blue fluorescence in ultra-violet light on dipping a strip of filter-paper into a hydrochloric solution of the liquid and adding a few drops of dilute sodium hydroxide solution. Podophyllin, which is sometimes added, may be detected in the lower parts of the paper by its strong yellow-green fluorescence. Boldine may be determined by dissolving it in a little alcohol, diluting with water, and titrating with hydrochloric acid, using methyl orange as indicator; its titre corresponds with that of a monacid base of formula $C_{19}H_{21}O_4N$. The residue of the ethereal extract from 40 kg. of leaves gave 1·54 per cent. of unsaponifiable matter, from which was obtained by repeated steam-distillation 0·28 per cent. of a fragrant yellow oil containing isocineole and phenols of high b.p. The distillation residue contained cedrene (b.p. 261°–270° C.). From the alkaline saponified solution there were separated fatty acids containing oleic, linolic, linolenic and saturated acids, and the unsaponifiable matter contained sitosterol. E. M. P.

Reaction for the Para-Amino Phenol Grouping and a Sensitive Test for Dulcin in the Presence of Saccharin. H. J. Vlezenbeek. (*Pharm. Weekblad*, **1937, 74,** 127–134.)—If saccharin is heated with resorcinol in the presence of strong sulphuric acid and the mixture is then diluted and made alkaline, a weak orange-red colour having an intense green fluorescence (due to sulphofluorescein) is visible by transmitted light (Börstein reaction). The sensitiveness is 1 mg. of saccharin in 5 to 6 litres of water, but the reaction is not specific, being given by *o*-phthalic acid, barbituric acid, etc. The reaction proposed by the author is based on Ekkert's test for phenacetin (*Pharm. Zentr.*, 1928, p. 99) in which 10 mg. are heated with 10 mg. of resorcinol in 2 ml. of strong sulphuric acid until a red colour results, the cool mixture being diluted with 10 ml. of water and divided into 2 portions, one of which is made alkaline with 10 per cent. ammonia and the other with sodium hydroxide solution. A phenolphthalein-red colour with a red-brown fluorescence is obtained with both reagents, but the latter produces a violet shade after 5 to 10 minutes. If an oxidising agent (*e.g.* a solution of iodine in alcohol, cupric sulphate, silver nitrate, bromine, potassium persulphate or mercuric oxide) is now added to the alkaline liquid, the fluorescence disappears and a dark violet colour appears immediately; this also develops in the absence of any oxidising agent if the alkaline liquid is allowed to stand overnight. The best conditions for heating in acid are usually 1·5 to 2 minutes at 180° C., but for some substances (*e.g.* holocaine hydrochloride) 200° C. is preferable, and with acoïn the acid should be boiled. Alternatively, the sample is heated with hydriodic acid (sp.gr., 1·70), the mixture being then made alkaline and resorcinol and iodine solution added. Positive reactions are also obtained with the following compounds, all containing the *p*-aminophenol grouping:—Citrophen, metol, salophen, methacetin, *p*-anisidine, *p*-phenetidine, phenocoll hydrochloride, dulcin, lactophenin (green fluorescence), cryofin (green fluorescence), glycine and *p*-acetamino-phenyl-allyl ether.

The *o*- and *m*-amino-phenols give a light green colour with copper sulphate, with iodine the former gives a wine-red colour turning to brown and the latter does not react. Mixtures of the three isomers give the reactions of the *p*-compound. Aspirin, caffeine, pyramidone and codeine hydrochloride show the green fluorescence on addition of alkali, but no change of colour on oxidation; carbohydrates interfere and must be removed. *p*-Nitrophenol, which gives an intense red colour and a red-brown fluorescence with the alkali, but no change with iodine and a purple-red colour with copper sulphate, gives, after reduction, the same reactions as *p*-amino-phenol. *p*-Phenylene-diamine gives a negative reaction with copper sulphate but, with iodine, an orange-yellow precipitate which dissolves slowly forming a violet solution. Negative results are obtained with aniline, acetanilide, *p*-nitraniline, phenol, hydroquinone, *p*-toluidine and arsacetin. Orthoform gives a wine-red colour turning brown with iodine (green with copper sulphate), and neosalvarsan, sodium salvarsan and myo-salvarsan give an alkaline liquid having a light red colour and green fluorescence which is unchanged by either oxidising agent. One per cent. of dulcin may be detected in the presence of saccharin by heating 100 mg. each of the sample and resorcinol for 1·5 to 2 minutes at exactly 180° C. in sulphuric acid. After dilution with 5 ml. of water and addition of sodium hydroxide the alkaline liquid has the orange-red colour and green fluorescence of saccharin; oxidation and dilution with 100 ml. of water then produce the violet colour due to dulcin. For use with mixtures the reaction is preferable to that described by Warenwet, in which the dulcin is tested directly with a fresh solution of lead peroxide or mercuric nitrate, and it is sensitive to 0·1 mg. of dulcin in 1 ml. J. G.

Determination of Bismuth in Quinine Iodobismuthate. M. François and L. Seguin. (*J. Pharm. Chim.*, 1937, **25**, 341–345.)—The original method for the determination of bismuth (François and Seguin, *J. Pharm. Chim.*, 1925, **2**, 59) sometimes gives too low results, and the following modification is therefore proposed:—About 1 g. of the sample is mixed in a warm 150-ml. beaker with 10 ml. of acetone, and stirred with a mixture of 5 ml. of a 20 per cent. solution of tartaric acid and 5 ml. of 30 per cent. sodium hydroxide solution (free from halogens). When the acetone solution is completely decolorised, 20 ml. of water are added, the mixture is heated on the boiling water-bath for half-an-hour, allowed to cool and filtered into a conical 375-ml. flask, and the precipitation vessel and filter are washed three or four times with a total volume of 50 ml. of water. After the addition of 125 ml. of 16 per cent. ammonium carbonate solution the filtrate is heated for 4 hours on the boiling water-bath and left for 24 hours. The precipitated bismuth carbonate is washed by decantation, and then filtered off, dried, ignited and weighed as oxide. The atomic weight of bismuth is now taken as 209, instead of 208, as in the original method. Results for various carefully dried salts were close to the theoretical and higher than in the original method (in which the sample is suspended in the alkaline tartrate solution and acetone is not used). As the percentage composition of quinine iodobismuthate, which is readily hydrolysed, depends on the way it is prepared, the method should be standardised. It is suggested that the method devised by the authors (*loc. cit.*) should be put at the beginning of the article in the forthcoming Codex. E. B. D.

Pharmaceutical Colouring Agents. A Substitute for Bordeaux B. C. L. M. Brown. (*Pharm. J.*, 1937, **84**, 344.)—Since a 1 per cent. solution of Bordeaux B gives a precipitate with a solution containing the maximum dose of potassium bromide (30 grains in ½ fl.oz.), numerous dyes were examined to find a substitute for it and to ascertain which dyes are most suitable for colouring pharmaceutical preparations. Standard solutions (A), of the dyes in chloroform water containing 25 per cent. of glycerin were added to solutions containing the minimum (5 grains), and the maximum (30 grains) of potassium bromide in ½ fl.oz., respectively. Lissamine red 6BS and amaranth gave no precipitate with potassium bromide solution, did not fluoresce, and were stable to dilute acid. Lissamine red 6BS behaved like Bordeaux B with dilute alkali, while the tinctorial value of amaranth increased approximately 4½ times in alkaline solution; these are therefore considered to be the best single dyes to replace Bordeaux B. In acid media Lissamine red 6BS, amaranth or, preferably, a 19:1 mixture of amaranth and indigo carmine, could be used. In alkaline media, "Solution of carmine," amaranth, or amaranth and indigo carmine as above, are suitable. For amaranth, alone or in the mixture, the amount of dye to be used in alkaline media is one-fourth that used in acid media. E. B. D.

Commercial Use of Iso-propyl Alcohol. W. Meyer. (*Chem.-Ztg.*, 1937, **61**, 317–318.)—In 1929 the (German) State Council of Health came to the conclusion that iso-propyl alcohol should not be used in the preparation of foodstuffs and medicinal preparations (including brandy) for internal or external use, and a statement to that effect was published (*Pharm. Ztg.*, 1929, No. 58, p. 929) for the information of the trades concerned. Experiments made by these trades have indicated doses of at least 100 g. have no serious effects on the human or animal organism. In a further official statement (in August, 1936), it was made clear that the ban does not apply to cosmetics such as hair-washes and eau de cologne, but only to medicinal preparations and foodstuffs, and that it makes no distinction between human and animal subjects. The statement also points out that existing regulations dealing with the use of propyl or iso-propyl alcohol as a substitute for ethyl alcohol already cover many foodstuffs. J. G.

Biochemical

Calcium-content of Blood Plasma and Serum. H. Thelen. (*Hoppe-Seyler's Z. phys. Chem.*, 1937, **246**, 194–202.)—The determination of the calcium in blood plasma and serum by precipitation as oxalate, both with and without previous treatment with heparin, was found to give valuable results. The author preferred to work on either the residue obtained by dry ashing or the solution obtained by digestion with a nitric-sulphuric acid mixture, both methods giving comparable results and agreement between duplicate analyses. With the modified technique the fluctuation of the calcium-content of plasma and serum as reported by Waelsch (*ibid.*, 1935, **234**, 27) was not substantiated, but an earlier report by Noguchi (to Nonnenbruch and reported in *Med. Klinik, Prager Ausgabe*, **1937**, **2**, [I]) was confirmed, and no material difference was found between the amount of calcium in the plasma and in the serum. S. G. S.

Contribution to the Biochemistry of Fluorine. II, Fluorine Estimations in Blood and Water. K. Kraft and R. May. (*Hoppe-Seyler's Z. phys. Chem.*, 1937, **246**, 233–243).—The fluorine solution was prepared by the method of Kolthoff and Stansby (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 118). The comparison solution was prepared by the addition of a solution of 160 mg. of zirconium oxychloride in 970 ml. of 6 *N* nitric acid solution to one containing 9 mg. of purpurin in 30 ml. of alcohol. The standard fluorine solution was made by dissolving 44·2 mg. of sodium fluoride (20 mg. of fluorine) in a litre of 8 *N* nitric acid. In the titration method it was necessary to work under constant conditions, especially when the colours were compared. The solutions were therefore made weakly alkaline before evaporation, and the cold dry residue was dissolved in 10 ml. of the zirconium solution. If the concentration of sodium chloride was too high and crystallisation took place, the solution was filtered through sintered glass into a measuring cylinder, and the filtrate, which usually amounted to 9·5 ml., was compared with an equal quantity of zirconium solution in glasses of equal width. The values found were calculated back to 10 ml. A first estimation was made by running the standard solution into the reagent glass until an approximate match was obtained. This was followed by a second estimation, in which a more precise measurement was made. Control determinations were made on the reagents, and when allowance was made for the fluorine-content of these, the error was less than 1γ when the amount present was between 10 and 40γ.

In the distillation method the apparatus consisted of the usual type for steam-distillation, except that the head of the distillation flask had a ground-glass joint and the receiver consisted of a tube with an overflow tube allowing the distillate to overflow into a porcelain dish. The steam-tube and the thermometer both passed to the bottom of the distillation flask. The temperature during distillation was kept at between 130° and 140° C. A higher temperature caused sulphuric acid to distil, and this affected the zirconium-purpurin lake, while at a lower temperature all of the silicofluoric acid did not distil. The distillation flask contained 20 ml. of distilled water and 20 ml. of pure conc. sulphuric acid. The mixture was cooled in ice and then 100 to 120 mg. of ground glass (coarse and fine) which had been extracted with conc. nitric acid, washed and ignited, were added. The solution under test was then added. The receiver contained 1 ml. of distilled water and sufficient 2 *N* sodium hydroxide solution to cause the distillate to be alkaline throughout the period of distillation. This was controlled by the addition of a drop of phenolphthalein solution. The distillate overflowed through the tube into the porcelain dish, which stood on a water-bath, so that a continual operation was obtained. The burners were so regulated that 180 ml. of water evaporated from the steam-boiler in 2 hours and that the temperature in the distillation flask did not vary much from 135° C. When the distillation was complete, the contents of the receiver were emptied into the porcelain dish, and the solution was evaporated to dryness and titrated as previously described. Fluorine was also obtained from the reagents and the apparatus, so that a carefully controlled blank estimation was required. When this was made and allowed for, the error amounted to 5 per cent. for 40γ of fluorine and to 10 per cent. for 20γ of fluorine.

The ashing of organic materials must be conducted with care to avoid loss of fluorine. Blood or serum, in quantities of 25 to 35 ml., was treated with 2 *N* sodium hydroxide solution in a porcelain dish, warmed over a small flame, heated in a muffle-furnace until the mass had blackened, and then calcined at a red heat. If the ash was then grey, it was scraped out of the dish, and any still adhering to the dish was rinsed out with water into a platinum crucible. After evaporation of this water the main portion of ash was added and incineration was completed in the platinum crucible. Finally, the ash was transferred to the distillation flask and heated with water until a clear solution was obtained. The presence of small carbon particles caused low values to be obtained. (*Cf.* Barr and Thorogood, ANALYST, 1934, **59**, 378.) S. G. S.

Effects of Tea and Wine on Enzymes. A. Zlataroff and I. D. Poppoff. (*Z. Unters. Lebensm.*, 1937, 154–164.)—The action of tea, red wine, white wine, caffeine and tannin on lipase, pepsin, trypsin, salivary amylase, oxidases, invertase and urease was investigated. The tea used had the percentage composition, water 9·96, caffeine 3·75, tannic acid 14·01, ash 5·72, nitrogen 5·05, ethereal extract 0·85, and water soluble components 36·75. Four g. of tea containing 3·75 per cent. of caffeine and 14·0 per cent. of tannin were infused for 10 minutes with 700 ml. of boiling water and filtered, and the filtrate was placed in 8 sterilised 100-ml. conical flasks which were then again sterilised for half-an-hour in a Koch's steriliser. One hundred ml. of the infusion contained 0·053 g. of tannin and 0·014 g. of caffeine. The red and white wines used contained 8·35 and 9·63 per cent. of alcohol, respectively (full analyses are given), and to ensure their composition remaining constant during the whole experiment they were kept at 0° C. for 10 days, then filtered through an asbestos filter, and kept in closed flasks at 10 to 15° C. For the investigations with caffeine and tannin, quantities of 0·01, 0·1, 1·0 and 5·0 ml. of 1 per cent. aqueous solutions were added to the enzyme-containing liquids. Control experiments were carried out with each group of tests.

It was found that even small quantities of tannin reduced the activity of lipase in unbuffered solutions, 5 ml. completely inhibiting it, but in buffered liquids small quantities were inactive and larger quantities caused a slight increase in enzymic activity. Caffeine was inactive in all concentrations.

At low concentrations tea, red wine, white wine, tannin and caffeine did not affect pepsin; at higher concentrations tea reduced the enzymic activity, whilst caffeine slightly increased it. With trypsin, in both buffered and unbuffered solutions, small quantities of tea and of both wines were inactive, whilst larger quantities appreciably reduced enzymic action. Even small quantities of tannin reduced the activity, larger quantities inhibiting it. Caffeine was inactive in unbuffered solutions and slightly increased the enzymic action in buffered solutions. Caffeine was inactive towards amylase at all concentrations both in buffered and unbuffered solutions. Tea, wines and tannin reduced the enzymic activity at low concentrations and inhibited it at higher concentrations. More than 0·1 ml. of the tea infusion or of wine, and all quantities of tannin, inactivated oxydase; more than 0·1 ml. of caffeine slightly increased the enzymic activity. Tea, wine and tannin inhibited the action of peroxydase, and caffeine increased it. Tea and wine inactivated blood catalase, larger quantities inhibiting the action in unbuffered liquids; small quantities of tannin reduced the action and larger concentrations inhibited it; caffeine slightly reduced the action in unbuffered media, but had no appreciable action in buffered liquids.

Tea and wine (the wine used was boiled for 3 or 4 minutes) reduced the activity of invertase, red wine being more active than white wine; tannin reduced the activity at low concentrations and inhibited it in larger quantities; caffeine was inactive.

With urease tea and wine were inactive in small quantities and reduced the enzymic action at higher concentrations; the inactivating effect was smaller in buffered liquids. Tannin had an inactivating action, large quantities inhibiting the action of the enzyme in unbuffered media. Caffeine had no effect on the enzyme. Experimental details and tables of results are given in the paper. E. M. P.

Diazo-reaction of Albumin and its Utilisation in Urology. E. Justin-Mueller. (*J. Pharm. Chim.*, 1937, **25**, 62–69.)—Into a test-tube, three-quarters filled with the sample of urine, are introduced 4 to 5 drops of a 1 per cent. solution of sodium nitrite, and exactly 3 drops of the reagent. This is prepared by dissolving 1 g. of β-naphthol and 0·9 g. of a 29·93 per cent. solution of sodium hydroxide (sp.gr. 1·33) in 50 ml. of water, to which is then added sufficient water to make 100 ml.; it is essential that this reagent should be clear, and it is therefore filtered, if necessary, just before it is used. The mixture is then shaken so as to produce a froth, and 10 drops of a mixture of 10 ml. of hydrochloric acid (sp.gr. 1·18) and 90 ml. of water are added on top of the froth. The following effects are obtained with urines containing (*a*) no albumin, (*b*) traces (*e.g.* 0·3 g. per litre), and (*c*) large quantities (*e.g.* 3 to 7 g. per litre), respectively. The froth is (*a*) small in quantity and colourless or dirty; (*b*) more abundant and white at the top and cherry-red below; (*c*) very abundant and similarly coloured. After a few seconds it (*a*) subsides and becomes dirtier; (*b*) becomes compact, and azure-blue at the top and blue-violet below; and (*c*) is greater in quantity and shows the same gradation of colours although these are more intense. The zone of separation between the froth and liquid is (*a*) absent; (*b*) just perceptible; and (*c*) very sharp and grey in colour. The liquid below the froth is yellow gold in all cases, although if the albumin-content is high, the lowest portion of the liquid shows no change in colour. It is important that the above technique should be followed exactly and the reaction is then preferable to the biuret test, especially for small quantities of albumin, inasmuch as it can be used with turbid or frothy liquids. The stability of the zone of separation is a characteristic feature of the test, and appears to be due to the formation of a gel by the action of the nitrous acid on the albumin. Strictly speaking, the reaction is not of the true diazo type, the naphthol being converted into a nitroso derivative and then into a naphtholic quinone oxime; the cherry-red colour obtained probably corresponds with a stage intermediate between these. In the presence of urea a Bordeaux-red precipitate is sometimes produced by this reaction at the zone of separation; this is attributed to liberation of nascent oxygen from the nitrous acid in the presence of hydrochloric acid, followed by condensation with two molecules of the nitroso- or quinone oxime compound. J. G.

New Method for Measuring the Decolorisation of Methylene Blue by Dehydrogenating Enzymes. H. J. Pistor. (*Hoppe-Seyler's Z. phys. Chem.*, 1937, **246**, 248–257.)—The author has used a Zeiss step-photometer, with the dark-green filter S53 and special photometer tubes, for the measurement of the colour of methylene-blue solutions. The decolorisation of the dye solutions was brought about by suspensions of *Acetobacter peroxydans* acting as a dehydrogenating enzyme. Colour readings were taken at frequent intervals and curves were plotted.

NOTE BY ABSTRACTOR.—The value of this paper appears to be in the modifications of the photometer rather than in the actual estimation reported.

S. G. S.

Spectrophotometric Studies of the Colour Development in the Analysis of Sugar by the Benedict Method and of Cholesterol by the Liebermann-Burchard Reaction. F. W. Sunderman and J. Razek. (*J. Biol. Chem.*, 1937, **118**, 397–404.)—Modern practice favours the use of a limited wave-band in colorimetry. In choosing a suitable band for any given liquid, constancy as well as intensity of absorption should be considered. Some liquids undergo changes of colour after their preparation, and absorption may vary in different degrees in different spectral regions. In the determination of sugar by Benedict's method (*J. Biol. Chem.*, 1931, **92**, 141) and of cholesterol by the Liebermann–Burchardt reaction changes of this kind occur and have been studied by the authors. The apparatus consisted of a high-voltage mercury or helium lamp of special design, used with a Rezek–Mulder colour analyser. This instrument is an automatic, photoelectric, indicating and recording spectrophotometer, by means of which the transmission curve of a given solution may be photographed over the visible range within 10 seconds. Although both the sugar and cholesterol solutions varied in colour during the period of observations, each type of solution exhibited constancy in transmission at a characteristic portion of the spectrum. The region of greatest constancy was found to be between 590 and 595$m\mu$ for the sugar solutions, and at 530$m\mu$ for the cholesterol estimation. With the latter the absorption in this zone was minimal and the procedure required modification either by increasing the concentration of cholesterol or by increasing the depth of the solution examined. The preferred procedure was to use the zone at 650$m\mu$ and to examine the colour after 20 minutes when absorption was nearly maximal. S. G. S.

Unsaponifiable Matter of Fish-liver and Fish-body Oils. S. Ueno and S. Nakaguchi. (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 85–86B.)—In work extending over several years the authors have noticed that when fish-liver oils contain much vitamin *A* the proportion of cholesterol is comparatively small, and they have now examined a further number of fish oils in order to determine whether the fact has any biological significance and whether it is of general application, *i.e.* whether it applies also to the fish-body oils. The liver and body oils of the following fish have been examined for sp.gr., n_D^{40}, saponification, iodine and acid values, unsaponifiable matter, cholesterol in the oil, and "blue number":—*Stromateoides argenteus; Psenopsis anomala; Caranx equula; Coryphaena hippurus; Dorosoma thrissa; Leiognathus argentea; Euthyopteroma virgatum; Platycephalus indicus* and

Taius tumifrons. In every instance the percentages of unsaponifiable matter, of cholesterol and of vitamin *A* were greater for the liver than for the body oils. The proportion of unsaponifiable matter other than vitamin *A* and cholesterol in the total unsaponifiable matter is greater in the body oils. Further, it appears that in the liver oils the ratio of the sum of vitamin *A* and cholesterol to the whole unsaponifiable matter varies between two fairly narrow limits, but such relationship seems doubtful for the body oils. An examination of a larger number of species is required to elucidate these points. D. G. H.

Quantitative Distribution of Ascorbic Acid in the Developing Barley Embryo. D. Glick. (*Compt. rend. Lab. Carlsberg,* 1937, **21**, 203–209.)—The embryo at varying stages of development was dissected from the remainder of the grain, weighed and ground in a micro-glass mortar with sand and 9·2 c.mm. of 2 per cent. metaphosphoric acid in *N* sulphuric acid. After grinding, 112 c.mm. of 1·8 to 1·9 per cent. metaphosphoric acid were added, the whole was stirred and centrifuged, and 91 c.mm. were used for titration with the dye solution, which was standardised so that each c.mm. was equivalent to 0·20γ of ascorbic acid. When the inner greenish-yellow leaf came out of the seed the concentration of ascorbic acid in it increased rapidly, and at the same time that in the coleoptile decreased. The coleoptile was relatively non-pigmented. The rootlet tips, which had the same greenish-yellow colour as the leaf and which showed plastids containing starch, were likewise richer in ascorbic acid than the non-pigmented rootlet. The values for the whole embryo rose until the second day and then fell, apparently owing to the increasing proportion of rootlet stem and coleoptile, which were low in ascorbic acid. A slight rise about the fifth day was probably due to the suddenly increasing concentration in the leaf. The embryo deprived of rootlet and leaf had a slightly increasing concentration throughout the period of observation. The values obtained on the inner leaf increased from 0·3 mg. per g. on the fifth day to just over 0·6 mg. per g. on the tenth day. Other values ranged from 0 to 0·3 mg. per g. S. G. S.

Contribution to the Study of Marine Products. Presence of Stigmasterol in Molluscs. W. Bergmann. (*J. Biol. Chem.*, 1937, **118**, 499–501.)—In addition to ostreasterol, small amounts of stigmasterol have been found in the oyster, *Ostrea virginica.* The stigmasterol-content is not constant, but apparently undergoes seasonal variations. Sometimes it is present in such small quantities that it can hardly be detected, while occasionally it has been found to represent as much as 4 per cent. of the total sterols. This sterol was identified as the acetate and tetrabromoacetate. S. G. S.

Bacteriological

Production of Milk of Abnormal Composition by Animals free from Udder Streptococci. E. G. Hastings and B. A. Beach. (*J. Agric. Research,* 1937, **54**, 199–220.)—It is generally held that about 90 per cent. of the cases of chronic mastitis are due to *S. agalactiae* (*S. mastitidis*) and the remainder to other bacteria; that *S. agalactiae* grows only in the udder; that it is carried from the infected to uninfected udders, the most frequent vehicle being the milker; that the infected quarters do not produce a proportionate amount of milk; that the disease shortens the milk-production period; that the milk produced by infected quarters is changed in composition; and that *S. agalactiae* is not pathogenic for man. In this paper an abnormal condition of the milk of a herd of cows is considered which was not due to chronic mastitis. The herd was one of 31 Holstein-Friesian heifers, free from tuberculosis and Bang's disease, which came to their first lactation period about one year after the animals were assembled primarily for the study of pasture management. The criteria used in classifying the milk as abnormal were a *p*H of 6·8 or above, a catalase value of 50 or above, and a chlorine-content of 0·15 per cent. or above, the milk being considered abnormal when any two of these conditions obtained. The highest figures recorded were *p*H = 7·0, catalase value 287 and chlorine 0·392 per cent. As many as 3100 samples were examined and all were free from *S. agalactiae.* Fourteen of the 31 cows were classed as definitely abnormal; these were specially investigated, and the yield, catalase, *p*H, acidity, chlorine, and bacteria per c.c. in fore-milk and whole-milk are recorded for each quarter of the udder. The abnormalities noted were such as to indicate a chronic inflammation of low intensity. A detailed examination as to the kind and number of bacteria was made. In general, the number of bacteria present in the abnormal milk was greater than that in the normal, but the types of bacteria present were apparently normal udder forms. It is suggested that the abnormal condition was due to this general increase of the normal bacterial content of the udders, but no explanation for this increase was found; a further study of a similar condition is being made. D. R. W.

B. Coli Test in Pasteurisation Control. M. H. McCrady. (*Milk Inspector,* 1936, **5**, 28–29; *Bull. Hyg.*, 1937, **12**, 295.)—The virtue of the test for *B. coli* as supplementary to the plate count lies in the fact that (1) *B. coli* is always present in raw milk, (2) it multiplies rapidly, outgrowing other types of bacteria, (3) it is easily detected even when present in very small numbers, and (4) it is practically eliminated by efficient pasteurisation. It is therefore very useful as a test for efficiency of pasteurisation and for re-contamination after pasteurisation. If pasteurisation reduces the *B. coli* count, it is at once assurance that the pathogenic bacterial count has been reduced. When the plate count reveals a lowered efficiency the *B. coli* test may be used to indicate whether there have been present thermophilic bacteria or whether there was an actual breakdown in the efficiency of pasteurisation. Re-contamination of the machinery has been found to be a very important item in pasteurisation control; the *B. coli* test is of great value in locating such contamination by the examination of samples taken at various points in the plant. D. R. W.

Isolation of *Brucella Abortus* from the Milk of Cows with Negative Blood Reactions to Agglutination Tests. T. M. Doyle and F. Beckett. (*J. Comp. Path. and Therap.*, 1936, **49**, 320–27; *Bull. Hyg.*, 1937, **12**, 309.)—The blood of 684 cows in 17 dairy herds in the south of England was tested, and 35 per cent. were found to agglutinate *Br. abortus* at a titre of 1 to 25 or over. The milk of the remaining 309 non-reacting cows was tested for the presence of *Br. abortus* by inoculation of guinea-pigs; it was found in only two. This confirms the findings of other workers that *Br. abortus* is rarely found in the milk of cows whose blood contains no agglutinins. D. R. W.

Isolation of the Influenza Virus and the Relation of Antibodies to Infection and Immunity. L. Hoyle and R. W. Fairbrother. (*Brit. Med. J.*, 1937, 655.)—The Manchester influenza epidemic of 1937 afforded an opportunity, of which the authors took advantage, for the isolation of the virus and a study of the relation between the presence of antibodies and protection. The virus was isolated in 13 cases by instilling saline broth washings of the upper respiratory passages and material expectorated directly from the trachea intra-nasally into ferrets. There are two related but distinct strains of the influenza virus—human and swine. The human strain only has been isolated from human influenza; the swine strain is responsible for the swine influenza of the Middle West States of America. In view of the frequent presence of antibodies against the swine virus in human adults, it has been suggested that the pandemic of 1918–19 was due to the swine variety. Both strains have a common antigenic factor, so that in complement-fixation tests antigens made from human and swine strains behave alike in fixing complement and thus preventing haemolysis. The two strains can, however, be distinguished by neutralisation tests, the virus + antiserum from an immunised ferret or human convalescent being without effect upon a ferret or mouse. By the complement-fixation test the authors have determined the amount of antibodies in the serum of convalescents and contacts and show that a high titre is generally found in the former, and that in the latter influenza developed only in those 5 individuals (out of 44 under observation) whose serum in a 1 in 2 dilution gave a doubtful or negative reading.

NOTE BY ABSTRACTOR.—This paper is of special interest as it indicates a new line of attack in the difficult study of ultra-microscopic micro-organisms.

D. R. W.

Toxicological and Forensic

Toxicological Study of Cobalt. M. F. Caujolle and S. Lafitte. (*J. Pharm. Chim.*, 1937, **25**, 351–371.)—Cobalt chloride solution ($M/10$) was injected into dogs at intervals up to 15 days, and the animals were then killed and the cobalt determined in the bile and in the various organs. The biological material was destroyed by Kahane's method (*cf.* Kahane, *Bull. Soc. Chim. Biol.*, 1932, **14**, 294; Kahane and Stefanesco, *id.*, 1933, **15**, 1239), and the cobalt was determined by Wassileef's method (*Z. anal. Chem.*, 1929, **78**, 439), involving separation as cobaltinitrite, oxidation of this with potassium permanganate solution, and titration of the excess of permanganate iodimetrically. The results, which are described in detail, show that cobalt accumulates in the liver and spleen, and to about the same extent as in the pancreas. The accumulation due to the intravenous injection of cobalt salts is not comparable with the cumulative effect of minute but long-continued administration of cobalt in food; the concentration of the metal in blood was very high in these experiments (*e.g.* 10·9 mg. per 100 g.), but was low after administration with a normal diet. The authors' results confirm the conclusion of Le Goff (*Compt. rend. Soc. Biol.*, 1928, **186**, 171, 1636; *Gaz. Hop.*, 1930, 978 and 1646) that cobalt is only slightly toxic. Symptoms that developed in one dog in the course of a fortnight were attributable to the amounts of cobalt injected being excessive. There were no special symptoms except, perhaps, acceleration of the heart's action. E. B. D.

Influence of Light on the Decomposition of Traces of Blood, with Special Reference to Medico-Legal Investigations. K. J. Hommes. (*Pharm. Weekblad*, 1937, **74**, 396–420.)—Samples of human and pig's blood were sprayed on to cotton, silk, tin, zinc, copper, silver, wood (painted and otherwise), filter-paper and calendered paper, and exposed to direct sunlight, diffused daylight, and in the dark for periods of 1·5 to 361 hours, 8 days to 10 months and 3 to 18 months, respectively. Bleaching was apparent after 1·5 hours in the sun, or 8 days in diffused light. The effects of subsequent exposure on the undermentioned tests were investigated; in no instance was any marked difference apparent between the behaviour of human and pig's blood. (1) *The guaiacum test.*—Exposure for a short time on zinc to sunlight or diffused light, or on silk for 185 hours in sunlight, invalidates this test, but satisfactory results are obtained under all conditions with all the other base materials mentioned. (2) *The haemochromogen and haemin crystal reactions.*—For the former Takayama's test (*Bull. Soc. Chim. Biol.*, 1931, **13**, 1263) is preferred to that of Bertrand (ANALYST, 1932, **57**, 664); the sample is warmed gently with a mixture containing 5 ml. of 10 per cent. glucose solution, 10 ml. of 10 per cent. sodium hydroxide solution, 65 ml. of water and 20 ml. of pyridine. After exposure to the sun for 33 hours on silk or cotton, or for 185 hours on filter-paper, both reactions are weakened considerably. Positive results were obtained on all the materials after exposure for 18 months to diffused light or in the dark. (3) *The spectroscopic method.*—This enables the changes which occur on exposure to sunlight (cf. *supra*) to be followed closely, and the results are given in detail. (4) *Solubility in water.*—The solubility of blood exposed on zinc, copper, silver or painted wood decreases rapidly, whilst that of blood on silk or filter-paper increases. Defibrinated pig's blood was exposed in black crystallising dishes for 118 hours (April to August) at 20° C., to radiations from sunlight covering the range 290 to 2400$m\mu$, and isolated by means of a range of eight filters. The change in solubility was evaluated as follows:—(i) The sample was filtered, and the filtrate and washings were evaporated and ignited in the presence of nitric acid, the residue being extracted with sulphuric acid, which was heated until fumes were evolved. After dilution with 10 ml. of water, 8 ml. of a fresh cold mixture of 10 ml. of amyl alcohol and 5 ml. of N potassium thiocyanate were added, and the red colour removed by the alcohol on shaking was evaluated in a Pulfrich step-photometer. The decreases in the Beer-Lambert constant per unit of wave-length (which measured the decrease in solubility of the blood) were 0·021, 0·018, 0·050, 0·051, 0·359, 0·075, and 0·004 for the ranges 700 to 644, 644 to 578, 578 to 546, 546 to 509, 509 to 480, 480 to 400, and 400 to 290$m\mu$, respectively. (ii) Similar values obtained, after exposure for 52·5 hours, by measuring the colour of a 1·0 per cent. solution of the blood, showed corresponding variations, and in particular confirmed that the range 545 to 480$m\mu$ produces the greatest decrease in solubility.

Infra-red photography of blood-stains.—Practical details are given concerning the infra-red photography of blood-stains. Results obtained with a range of Agfa-plates (maximum sensitiveness ranging from 730 to 960$m\mu$) and filters are recorded and illustrated. The best results for stains on white rag and on dark brown wool were obtained with a 730$m\mu$ "hart" plate, and a 810$m\mu$ "rapid" plate, respectively, and with Filter No. 42. Ordinary and panchromatic plates were less successful. Curves relating the log. of the absorption coefficient of a solution of oxyhaemoglobin (crystallised in a vacuum at 0° C.) and the wave-length show a fall to a minimum between 600 and 680$m\mu$, followed by a rise to a maximum at 930$m\mu$, and another decrease to a low value at 1350$m\mu$; these results correspond with the optimum wave-lengths recorded for infra-red photography (cf. *supra*). The requisite values were obtained by means of a spectroscope provided with a tungsten lamp source and a vacuum thermo-element for transforming the heat of absorption into a galvanometer reading. J. G.

Agricultural

Proportions of Sulphur, Phosphorus and Nitrogen in Plants Cultivated in the same Soil. G. Bertrand and L. Silberstein. (*Bull. Soc. Chim.*, 1937, [5], 4, 760–761.)—Previous work on the proportions of sulphur, phosphorus and nitrogen in annuals, biennials and perennials grown in a chemically very homogenous soil (ANALYST, 1936, **61**, 201) has now been supplemented by the inclusion of celery, onion, lucerne, flax, burnet, bean, lotus, tomato, and potato, together with certain weeds (poa, groundsel, malva, etc.)—forty-seven kinds of plants in all. The ratio of sulphur to phosphorus is not above 4·02, and that of sulphur to nitrogen not above 0·5 in 46 of these, but in celery the proportions are very different, showing in a vegetative sample and in a flowering sample a ratio of sulphur to phosphorus of 11·117 and 7·500, respectively, and a sulphur to nitrogen ratio of 0·619 and 0·610. Before any conclusion is drawn, work is to be carried out to determine the forms under which the sulphur is stored in celery. D. G. H.

Acceleration of Digestion in the Kjeldahl Method as applied to Soil and Grass Analysis. F. L. Ashton. (*J. Soc. Chem. Ind.*, 1937, **56**, 101–104T.)—The author has compared Kjeldahl's original method with potassium permanganate (*Z. anal. Chem.*, 1883, **22**, 366), Subrahmanyan's method (*Mem. Indian Inst. Sci.*, 1935, **2**, 213; 1935, **3**, 35), and Beet and Furzey's method (*Fuel*, 1934, **13**, 343; *J. Soc. Chem. Ind.*, 1936, **55**, 108T). For the addition of the permanganate the technique was developed of cooling the flask for exactly 1 minute, dropping in 5 g. of potassium permanganate wrapped in a 9-cm. filter-paper, and replacing the flask on the digestion stand with its neck in the fume-extraction flue without further heating. In the Beet and Furzey method to 1 g. of grass 10 g. of the "mixture" (containing 0·26 g. of selenium, 1·32 g. of mercuric sulphate, and 8·42 g. of potassium sulphate) and 20 ml. of conc. sulphuric acid were added; digestion was continued for 10 minutes after clearing. Owing to the design of the apparatus it was necessary to add the sodium sulphide immediately before connecting the distillation flask with the condenser. The ammonia was received in 0·1 N sulphuric acid instead of boric acid, as recommended by Beet and Furzey. For the soil analysis, 10 g. of soil, 30 ml. of acid, and 15 g. of "mixture" were used. In the investigation of Subrahmanyan's method the author's instructions were followed as closely as possible. Preliminary experiments showed that the temperatures of digestion depend more on the proportion of salts to acid than on any other factor. The quantity of selenium has little effect on the rate of digestion, 0·2 g. being sufficient for 10 g. of soil. Increasing the proportion of sodium sulphate increases the rate of digestion. Reduction of the quantity of acid causes loss of nitrogen. The results of a comparison of Subrahmanyan's method with various modifications of the Kjeldahl method for soils are given in a table. Another table shows the results obtained by Beet and Furzey's method with 20 minutes' digestion and by the sodium sulphate and selenium method with 90 minutes' digestion.

The general conclusions drawn are that the potassium permanganate method can be used for soils when results are required quickly and a high standard of accuracy is not needed. Subrahmanyan's method gives with soils figures comparable with those obtained by other methods, but has few advantages to recommend it; it gives low results with grass. Beet and Furzey's catalyst is more efficient than selenium and sodium sulphate with soils, but when the quantity of acid is reduced to make it effective, losses of ammonia occur; with grass it is very satisfactory, reducing the time of digestion from 90 minutes to 20 minutes. E. M. P.

Determination of Small Amounts of Sodium in Soil Solutions, Extracts, etc. B. T. Mulwani and A. G. Pollard. (*J. Soc. Chem. Ind.*, 1937, **56**, 128–129T.)—Sodium may be determined in soil solutions by the colorimetric method of McCance and Shipp (ANALYST, 1931, **56**, 552), with an accuracy nearly as great as with Blenkinsop's volumetric method (ANALYST, 1931, **56**, 134). Further, there is a considerable saving in time, and a wider range of sodium concentrations may be covered. A detailed examination of the McCance method has been carried out under the conditions met with in soil solution analysis. The method is more sensitive to the presence of potassium than the volumetric method, probably because the triple salt is precipitated in 50 per cent. alcohol, but excessive amounts of potassium may be removed by pre-treatment with perchloric acid. In experimental tests, in which 0·1, 0·5, 1·0, 1·5 and 2·0 mg. of potassium were added to solutions containing 0·0786 mg. of sodium, the volumetric method gave trustworthy results in the presence of approximately 12 times, and the colorimetric method in the presence of about 4 times as much potassium as sodium. The large excess of calcium in soil solutions ensures that no water-soluble phosphate remains after gentle ignition of the residue from the evaporation of the test solution. Alternatively, the phosphate may be removed by precipitation with alcoholic zinc acetate and hydroxide and centrifuging. To ascertain the safety limit of acidity for the use of the colorimetric method in the examination of acid solutions of soil, solutions containing 0·0786 mg. of sodium were acidified with hydrochloric acid. With a concentration of 4·5 N recovery was nil; with 2·2 N and 1·1 N solutions recovery was practically complete. The effect of various soil bases was tried, *e.g.* with solutions containing, in addition to the 0·0786 mg. of sodium, calcium 20, magnesium 2, iron 0·2, aluminium 0·2 and manganese 0·4 mg., and in each test recovery of the sodium was satisfactory. For very small amounts of sodium the precipitate of triple salt was dissolved in a minimum amount of water, and the ferrocyanide colour was developed in 5 ml. instead of 25 ml.; in this way amounts of 0·002 to 0·02 mg. of sodium chloride were satisfactorily determined. D. G. H.

Identification of Tephrosin and Deguelin from different Sources. J. J. Boam, R. S. Cahn and A. Stuart. (*J. Soc. Chem. Ind.*, 1937, **56**, 91T–96T.)—The authors give a table of the m.p. and other characteristics of tephrosin claimed to have been isolated from natural sources from 1907 to 1936. It is shown that tephrosin, *allo*tephrosin, and *isoallo*tephrosin are identical, and also that *iso*deguelin (Merz, *Arch. Pharm.*, 1932, **270**, 362; Merz and Schmidt, *id.*, 1935, **273**, 1) is identical with deguelin. Merz's dihydrodeoxy*iso*deguelin is a new substance and should be renamed dihydrodeoxydeguelin; dihydro*isoallo*tephrosin, also new, should be renamed dihydrotephrosin (of which dihydro*isoallo*tephrosin is an impure form). The differences in m.p. found by different observers appear to have no relation to the purity of the products; crystallographic data are necessary for the identification of these substances. The authors give the results of their re-determination of the optical data of tephrosin, deguelin and dehydrodeguelin, and have also determined the constants of the substance melting at 189° C. isolated by Cahn and Boam from Sumatra-type derris root; this substance, which is not identical with tephrosin, has been named *sumatrol.* Data are given for only one form of sumatrol; the high-melting form, which was obtained several times in the original preparations, has not been obtained in later work.

For the preparation of tephrosin and deguelin the published methods were followed in general. The following method is given for the treatment of tephrosin with ammonia. The tephrosin (0·5 g.), m.p. 190 to 191° C., just dissolved in 40 ml. of boiling absolute alcohol; on cooling, crystals separated, but these had the same m.p. as the original material. After 3 hours 20 ml. of the supernatant solution were decanted and saturated with dry ammonia at room temperature; the solution became pale yellow and deposition of crystals began immediately; after standing overnight, they were collected, and then had m.p. 193° C. and gave Durham's reaction (indicating the presence of deguelin). To the remaining 20 ml. of solution and the separated crystals (m.p. 190 to 191° C.) sufficient hot absolute alcohol (15 ml.) was added to dissolve them, and dry ammonia was passed into the solution while it was cooling. Next morning the crystals were filtered off from the yellow solution; they melted at 198° C. and did not give Durham's reaction. Concentration of the mother liquor gave a further yield of crystals which, after recrystallisation from chloroform and methyl alcohol, had m.p. 197°–198° C. and did not give Durham's reaction.

Deguelin appears under the microscope as colourless elongated prisms. Tephrosin is colourless and under the microscope is similar in appearance to deguelin. Dehydrodeguelin crystallises in very fine needles, colourless or pale yellow. Sumatrol crystallises from acetone or alcohol in fine needles with a tendency towards a bladed form; the crystals are probably triclinic. Optical crystallographic data for these four substances are given, with diagrams. E. M. P.

Organic

Tests for Carbon Monoxide and Nitrous Oxide in the Combustion of Organic Nitrogen Compounds. M. Badoche. (*Bull. Soc. Chim.*, 1937, [5], **4**, 232–239.)—As occasionally a minute deposit of carbon remains after combustion of an organic compound in compressed oxygen in the calorimetric bomb, the author investigated the extent to which carbon monoxide and nitrous oxide might also be formed. The substances used included hexamethylenetetramine, nitroguanidine and aromatic nitro compounds. Carbon monoxide was tested for after the combustion by oxidation with heated iodine pentoxide and colorimetric determination of the iodine liberated; the amount of carbon monoxide formed was, however, minute, and was insufficient to give rise to an error of more than 1 part in 10,000 in the calorific value of the substance. Nitrous oxide was tested for by a method which involved concentration by condensation by means of liquid air and ultimately burning it with hydrogen in a eudiometer and measuring the contraction in volume; the amount formed was too small to be detected. S. G. C.

Determination of 8-Hydroxyquinoline by means of Potassium Bromate. E. Schulek and O. Clauder. (*Z. anal. Chem.*, 1937, **108**, 385–396.)—8-Hydroxyquinoline (20 to 40 mg.) is dissolved in hydrochloric acid in a flask, the stopper of which is surrounded by a cup. The solution is made alkaline with sodium hydroxide solution and, after dilution to about 50 ml., treated with 0·5 g. of potassium bromide. Sufficient $N/10$ potassium bromate solution is run in from a burette to ensure that there is an excess of from 10 to 20 per cent. Conc. hydrochloric acid (10 ml.) is added, the flask is immediately closed, and a solution of 3 g. of potassium iodide in 10 ml. of water is placed in the cup, after which the flask is placed in the dark for 5 minutes. The flask is cooled, and the potassium iodide solution is allowed to run in. After dilution of the mixture with about 300 ml. of water, the liberated iodine is titrated with $N/10$ sodium thiosulphate solution, starch being used as indicator. Each ml. of $N/10$ potassium bromate solution is equivalent to 3·6277 mg. of 8-hydroxyquinoline.

Separation of 8-hydroxyquinoline from other substances with which it is associated in pharmaceutical preparations can be effected by distillation but, owing to the amphoteric properties of the compound, it is necessary to distil from a medium strongly buffered at *p*H 8. A portion of the preparation corresponding with 20 to 300 mg. of hydroxyquinoline is dissolved in 10 ml. of $N/10$ to N hydrochloric acid according to the amount of hydroxyquinoline present. The solution is made up to about 50 ml. with water, and to it are added 5 g. of crystallised sodium acetate or sodium potassium tartrate, a glass bead and a little powdered pumice. Distillation is carried out in an apparatus with ground-in glass connections, preferably that of Schulek and Vastagh (*Z. anal. Chem.*, 1934, **84**, 167), and is allowed to proceed until about four-fifths of the liquid has distilled. If necessary, 10 ml. of water may be added and the distillation continued. The small amount of hydroxyquinoline which appears in the condenser is washed into the receiver with acid.

Mixtures of hydroxyquinoline with phenacetin are shaken with dilute hydrochloric acid and the insoluble phenacetin is filtered off. The filtrate is made alkaline to methyl red, slightly re-acidified, made up to about 50 ml., buffered as previously described and distilled. Alternatively, the sample may be heated with 15 ml. of 3 per cent. sulphuric acid, the phenacetin extracted with chloroform or ether and the aqueous layer distilled as before. Hydroxyquinoline may be separated from pyramidone (which decomposes slightly into volatile products) by the distillation method, followed by re-distillation of the buffered distillate. A single distillation by the method described suffices for separation from sulphosalicylic acid. Either method is applicable to separation from the basis of an ointment or suppository. Separation from hexamethylene tetramine requires a special procedure, because formaldehyde forms a green condensation product with hydroxyquinoline. The sample, in a solution buffered as previously described, is extracted repeatedly with chloroform. The combined chloroform solutions are extracted with portions of a 5 per cent. solution of the buffer substance, and these aqueous extracts are again extracted with a little chloroform. All chloroform extracts are combined, mixed with a little *N* hydrochloric acid, shaken well and the chloroform is removed by evaporation. A. O. J.

Determination of *p*-Amino-benzenesulphonamide. E. Schulek and I. Boldizsár. (*Z. anal. Chem.*, 1937, **108**, 396–400.)—It has been shown recently (Trefouel, *Compt. rend. Soc. Biol.*, 1936, **120**, 756; Buttle, Gamb, Gray, and Stephenson, *Lancet*, 1936, **230**, 1286) that *p*-amino-benzene-sulphonamide may be used in the treatment of streptococcal infection with excellent results in place of the more toxic Prontosil and Prontosil-S of Domagk (*Deut. Med. Woch.*, 1935, **61**, 250). The substance forms white crystals melting, according to Allport (*Quart. J. Pharm.*, 1936, **9**, 560), at 166·5° C., and, according to the present authors, at 165° C. Its solubility in water is 1 part in 632 at 0° C., and 1 part in 240 at 15° C. It is very soluble in hot water. In neutral or weakly acid solutions, bromine water reacts with it to form a white or flesh-coloured precipitate, the reaction being sensitive. If *p*-amino-benzenesulphonamide is diazotised and coupled with phenol, the same colour is produced as if the reaction had been carried out with sulphanilic acid. Allport (*loc. cit.*) reports that it may replace sulphanilic acid in the Griess–Ilosvay reaction, but the colour produced is variable in shade and intensity. Owing to its amphoteric nature it cannot be isolated from acid or alkaline solutions by simple extraction with organic solvents. Its determination can be effected by means of its di-bromo substitution product. About 30 to 80 mg. are dissolved in acid and treated with *N*/10 potassium bromate solution (which should be in 10 to 30 per cent. excess), under the conditions and with the procedure described in the previous abstract, the iodine solution ultimately obtained being titrated with *N*/10 sodium thiosulphate solution. Each ml. of *N*/10 potassium bromate solution is equivalent to 4·304 mg. of *p*-amino-benzenesulphonamide. Errors in the determination of known amounts of the pure substance varied from +0·3 to +0·8 per cent. A portion of a preparation for injection containing 30 mg. of the sulphonamide and 450 mg. of ethylene glycol in 0·6 ml. gave results varying from 98·4 to 99·8 per cent. of the amount present. *p*-Amino-benzenesulphonamide, dissolved in 5 to 10 per cent. sulphuric acid, can also be determined by direct titration with standard potassium bromate solution after the addition of 1 g. of potassium bromide. The completion of the reaction is indicated by the appearance of a yellow colour which shows up distinctly against the silky white precipitate of the di-bromo compound. This method gives somewhat low results. A third method for the determination is by hydrolysis of the sulphonamide group. From 20 to 200 mg. are boiled for one hour with 5 ml. of 70 per cent. sulphuric acid beneath a reflux condenser having ground-in glass connections luted with conc. sulphuric acid. The condenser and connections are washed into the flask, the contents of which are made up to 50 or 60 ml. with water. After the addition of a few drops of methyl red solution and a little pumice, the liquid is distilled into a receiver containing, according to the amount of sample taken, 0·02 *N* or 0·1 *N* hydrochloric acid. When the air in the apparatus has been replaced by steam, 10 per cent. ammonia-free sodium hydroxide solution is run into the flask by means of a tap-funnel until there is an excess of from 0·2 to 1 ml. over the amount required to change the colour of the indicator. When two-thirds of the liquid has distilled, the condenser is washed into the receiver, the contents of which are boiled with a little pumice, cooled, and titrated with carbonate-free 0·02 *N* or 0·1 *N* sodium hydroxide solution. Each ml. of 0·02 *N* acid is equivalent to 3·4428 mg. of *p*-amino-benzenesulphonamide. The error of determination by this method varies from 0 to +1·2 per cent. A. O. J.

Essential Oil of *Phyllocladus alpinus*. L. H. Briggs. (*J. Soc. Chem. Ind.*, 1937, **56**, 137–138T.)—In continuation of the author's work showing dacrene and sciadopitene to be identical with phyllocladene (*J. Chem. Soc.*, 1937, 79) the essential oil of *Phyllocladus alpinus* has now been investigated. The volatile oil obtained on steam-distillation of the leaves solidified completely, on cooling, to a crystalline solid, which on re-crystallisation from methyl or ethyl alcohol, had m.p. 96·5° C., undepressed by a sample of authentic phyllocladene obtained from *Phyllocladus rhomboidalis*. It had a rotation of $[\alpha]^{25}_{D}$ + 15·8 in chloroform. The diterpene gave a faint but definite yellow colour with tetranitromethane, and with conc. sulphuric acid a yellow colour which, on addition of acetic anhydride, became dark brown with green fluorescence. It immediately decolorised a dilute solution of bromine in chloroform or glacial acetic acid, but not in ether. Isomerisation was complete in a few minutes on heating 50 mg. of the phyllocladene in 10 per cent. absolute alcohol to 100° C. The α- and β-dihydrophyllocladenes may be obtained by hydrogenating a glacial acetic acid solution of phyllocladene in the presence of Norit, adding water after removal of the catalyst, and crystallising the α-product (m.p. 73°–74° C.). The β-product (m.p. 55° C.) may be obtained from the mother liquors in small yield after re-crystallisation from methyl alcohol. The winter oil of *Phyllocladus alpinus* is solid at ordinary temperature, and consists almost entirely of the tetracyclic diterpene, phyllocladene. D. G. H.

Separation of Choline and Ethanolamine. E. Chargaff. (*J. Biol. Chem.*, 1937, **118**, 417–419.)—A solution of 1·94 g. of choline hydrochloride and 1·7 g. of ethanolamine hydrochloride in 9 ml. of water was treated with 4·7 g. of sodium bicarbonate and 10 ml. of chloroform. The mixture was then shaken with

4 g. of carbobenzoxy chloride* which was added in four portions. It is advisable to cool the reaction mixture in running water for the first 15 minutes. After 1 hour no more carbon dioxide was given off, and the mixture was acidified with dilute hydrochloric acid, more chloroform was added, and the two layers were separated. The aqueous layer was washed four times with chloroform. The united chloroform extracts were washed four times with very dilute hydrochloric acid and twice with water, dried with anhydrous sodium sulphate, and concentrated *in vacuo*. The remaining crude oil, weighing 4·2 g., was dissolved in 5 ml. of warm chloroform, and petroleum spirit (b.p. 30°–60° C.) was added until a turbidity developed. After 12 hours in a refrigerator long needles had crystallised, which weighed 1·98 g. and melted at 65·5°–66° C. On addition of petroleum spirit 0·45 g. of the same compound was obtained from the mother liquor. The total yield of 2·43 g. corresponded to 72 per cent. of the theoretical yield. After one more crystallisation from the chloroform and petroleum spirit, carbobenzoxy ethanolamine, $C_6H_5.CH_2OCONHCH_2CH_2OH$, was obtained as long colourless needles melting at 66·5° C. The absence of choline was confirmed by ultimate analysis and by a mixed melting-point test with a similar compound prepared from pure material. The free base was recovered by suspending 0·5 g. of the carbobenzoxy compound in 5 ml. of *N* hydrochloric acid and heating the mixture for 2 hours with hydrogen in the presence of palladium catalyst according to Bergmann and Zervás (*Ber.*, 1932, **65**, 1192); this caused it to dissolve. The syrup obtained on concentration *in vacuo* of the filtered solution was dissolved in 0·8 ml. of conc. hydrochloric acid, and a conc. solution of gold chloride in conc. hydrochloric acid was added. The gold chloride salt of ethanolamine crystallised immediately in yellow needles, which were filtered off, washed with chilled conc. hydrochloric acid and dried. The substance weighed 0·85 g. (80 per cent. of the theoretical amount), melted at 194°–195° C. (corr.), and was identical with the gold salt obtained from pure ethanolamine.

The aqueous layer containing the choline was diluted with water to exactly 200 ml., and aliquot parts were used for the estimation of choline and for the preparation of derivatives. By the micro-method of Roman (*Biochem. Z.*, 1930, **219**, 218), based on the formation of the enneaiodide of choline, $C_5H_{14}NOI_9$ (Staněk, *Z. phys. Chem.*, 1905, **46**, 280), a total of 1·75 g. of choline chloride was found, corresponding with 90·2 per cent. of the choline chloride originally present. From another portion of the aqueous solution the gold chloride salt of choline was prepared as fine yellow platelets, m.p. 274° C. (corr.). The choline was further characterised by the formation of the typical chloroplatinate and by the formation of nitrocholine perchlorate according to the method of Hofmann and Höbold (*Ber.*, 1911, **44**, 1766). It is claimed that this method of separating choline from ethanolamine is applicable to any solution containing them and may be extended to other substances containing free amino groups (*cf.* next abstract). S. G. S.

Method for the Isolation of Glucosamine. E. Chargaff and M. Bovarnick. (*J. Biol. Chem.*, **1937**, **118**, 421–426) (*cf.* preceding abstract).—A solution of 5·83 g. of glucosamine hydrochloride in 25 ml. of water was treated with 5·25 g. of sodium bicarbonate followed by 6·2 g. of carbobenzoxy chloride in five portions, with shaking, during the course of an hour. The mixture was kept in a refrigerator for a few hours, 25 ml. of chloroform were added to the white paste formed, and the precipitate was filtered off, washed with chloroform, and dried. It weighed 7·73 g. (99 per cent. of the theoretical yield). On re-crystallisation from 30 per cent. methyl alcohol white lancet-shaped needles were obtained which melted, with decomposition, at 214° C. (corr.). The substance was dextrorotatory and showed marked mutarotation, with a final $[\alpha]_D^{24} = +75{\cdot}4°$ in pyridine. It reduced Fehling's solution and gave a negative ninhydrin reaction. On treatment with palladium and hydrogen an almost quantitative yield of glucosamine was obtained.

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* Benzyloxycarbonyl chloride or benzyl chlorocarbonate, $C_6H_5CH_2·O·COCl$.

Glucosamine was also separated from a mixture of sugars by a similar procedure. A mixture of 2·0 g. of *d*-galactose, 2·0 g. of *d*-glucose, 1·0 g. of *d*-mannose and 1·3 g. of glucosamine hydrochloride was dissolved in 10 ml. of water; 1·5 g. of sodium bicarbonate and 2·0 g. of carbobenzoxy chloride (in two portions) were added, and the mixture was shaken for 40 minutes. After being chilled in the refrigerator, the precipitate which had formed was centrifuged off and thoroughly washed with ice-water. It was suspended in 45 ml. of 2 *N* hydrochloric acid and treated with hydrogen in the presence of the palladium catalyst for 6 hours, and the glucosamine hydrochloride was isolated as previously described. A similar method was used for the separation of glucosamine from glycine. A solution of 1·0 g. of glucosamine hydrochloride and 1·0 g. of glycine in 10 ml. of water was exactly neutralised with *N* sodium hydroxide solution, and 1·8 g. of sodium bicarbonate and 3·5 g. of carbobenzoxy chloride (in three portions) were added. Because of foaming the mixture was diluted with water to 50 ml., shaken for half-an-hour and chilled in a refrigerator. Almost pure carbobenzoxy glucosamine had precipitated. On acidifying the filtrate with hydrochloric acid carbobenzoxy glycine was obtained. The yields corresponded with 78 per cent. of the glucosamine hydrochloride and with 70 per cent. of the glycine taken. S. G. S.

Determination of Fumaric Acid in Protein Solutions containing Succinic Acid. E. Stotz. (*J. Biol. Chem.*, 1937, **118**, 471–477.)—Amounts of fumaric acid from 2 to 12 mg. may be determined with an accuracy of 3 to 5 per cent. by the formation of mercurous fumarate, which is then oxidised to mercuric fumarate, which in its turn is determined by thiocyanate titration. A 4-ml. sample of the unknown solution containing protein was delivered into a 15-ml. conical centrifuge tube, treated with 0·5 ml. of 25 per cent. trichloroacetic acid, and allowed to stand for 5 minutes. The mixture was centrifuged, the supernatant fluid was transferred to a second tube, the precipitate was washed twice with 2 ml. portions of hot ether, and the washings were added to the main liquid. A drop of saturated alcoholic methyl red solution was added, followed by alcohol until the whole was completely miscible. Hot saturated baryta solution was added slowly until the red colour changed to yellow. The tube was then completely filled with alcohol, thoroughly mixed, and allowed to stand for 30 minutes. The contents were centrifuged, the supernatant fluid was removed, and the precipitate was dissolved in 4 ml. of water and 2 ml. of 15 per cent. nitric acid. This solution was heated in a boiling water-bath, 1 ml. of mercurous nitrate reagent (10 per cent. of $HgNO_3$ in 5 per cent. nitric acid) was added, and the tube was simultaneously cooled and its walls scratched until crystallisation was induced. The tube was allowed to stand in a refrigerator for 2 to 4 hours (a longer time is advisable) and then centrifuged for 5 minutes. After the supernatant fluid had been drawn off, the precipitate was stirred with 2 ml. of a 15 per cent. nitric acid, and heated for a few minutes in a boiling water-bath. Four ml. of water and 1 ml. of mercurous nitrate reagent were added, and crystallisation was again induced. The tube was allowed to stand in the refrigerator for at least 4 hours, after which it was centrifuged. The precipitate was washed once with 5 ml. of a 1 per cent. solution of mercurous nitrate containing 5 per cent. of nitric acid, and twice with 5-ml. portions of 0·2 per cent. nitric acid. The washed precipitate was heated with 1 ml. of conc. nitric acid and stirred, and 5 ml. of water were added. Saturated permanganate solution was then added in excess until the purple colour was permanent, after which the tube was heated for a few minutes in a boiling water-bath. After cooling, a minimum quantity of 3 per cent. hydrogen peroxide solution was added to dissolve the manganese dioxide. The solution was then quantitatively transferred to a 100-ml. Erlenmeyer flask, and titrated with standard (approximately 0·02 *M*) ammonium thiocyanate solution, ferric ammonium sulphate solution being used as the indicator. S. G. S.

New Method for the Identification of Naphthol Yellow S and a Suggested Mechanism of its Fading. H. H. Hodgson and E. W. Smith. (*J. Soc. Chem. Ind.*, 1937, **56**, 108T.)—Contrary to the results of Lauterbach (*Ber.*, 1881, **14**, 2028) and Finger (*J. pr. Chem.*, 1909, **79**, 441) the authors have found that 2-nitro-4-amino-α-naphthol-7-sulphonic acid, prepared by dissolving 8 g. of Naphthol Yellow S (2:4-dinitro-α-naphthol-7-sulphonic acid) in a mixture of 20 ml. of hydrochloric acid (sp.gr. 1·16) and 250 ml. of water, and treating the solution for 30 minutes with 14·5 g. of stannous chloride, followed by a saturated solution of sodium acetate, crystallises from water in deep red-brown iridescent micro-prisms. Wool and silk can be dyed deep red-brown shades which are fast to acids and alkalis from a bath containing 0·5 g. of the sulphate of 2-nitro-4-amino-α-naphthol-7-sulphonic acid, 10 g. of Glauber's salt, 2 ml. of conc. sulphuric acid and 100 ml. of water; the wetted wool is introduced in the cold, the bath is heated to boiling in 30 minutes, and maintained at the b.p. for 45 minutes. The fastness of these colours can be used as an identification test for Naphthol Yellow S. When wool or silk dyed with this product is immersed in a cold dilute hydrochloric acid solution of stannous chloride the dye is reduced to the pale yellow hydrochloride of 2-nitro-4-amino-α-naphthol-7-sulphonic acid, which is dissociated on the fibre to the red-brown base when the material is washed. Treatment with acids changes the colour to pale yellow, which is changed to a very deep red by alkalis, with a certain amount of stripping; the colour is rendered fast by boiling the material with water. Experiments on these lines with wool dyed with Naphthol Yellow S which had been rendered brown by fading in sunlight suggested that during fading photo-reduction occurs on the fibre, with the probable formation of 2-nitro-4-amino-α-naphthol-7-sulphonic acid. Fading might be prevented by the presence of some agent that would prevent reduction. E. M. P.

Inorganic

Application of Tin Amalgam to the Analysis of Alloys. J. V. Tananaev and E. Davitashvili. (*Zavodskaya Laboratoriya*, 1936, 819–20.)—Tin amalgam is prepared by heating mercury with 8 to 10 per cent. of granulated tin under dilute hydrochloric acid. The reduction and titration must always be carried out in a stream of carbon dioxide. For the determination of copper in bronze, 0·2 to 1 g. of the alloy is decomposed by heating with 20 to 25 ml. of conc. sulphuric acid. The solution is boiled to remove sulphur dioxide, cooled, and made up with water to a definite volume. From 20 to 50 ml. are shaken with tin amalgam for 5 minutes at 60°–70° C., after which the amalgam is removed (method not stated), and the solution is titrated with potassium dichromate in presence of diphenylamine. One ml. of $N/10$ dichromate solution = 0·003179 g. of copper. S. P. S.

Determination of Gold by means of Hydroquinone. F. E. Beamish, J. J. Russell and J. Seath. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 174–176.)—Hydroquinone presents advantages over sulphur dioxide, ferrous sulphate, and oxalic acid in providing a better separation of gold from platinum and palladium. The gold solution is evaporated to dryness with sodium chloride, the residue is moistened three times with hydrochloric acid with intervening evaporation to dryness. The residue is dissolved in 15 ml. of water and 5 ml. of hydrochloric acid, diluted to 50 ml., heated to boiling, and gradually precipitated with a slight excess of a 1 per cent. aqueous hydroquinone solution. Boiling is continued for 20 minutes. After standing in the cold, the liquid is filtered through a porous porcelain crucible or close-grained filter-paper, and the precipitate is washed with hot water, care being taken to transfer the whole of the finely-divided metal. The sides of the beaker may be wiped with small pieces of ashless filter-paper. If palladium is present, it may be determined in the filtrate by direct dimethylglyoxime precipitation. For the determination of platinum, the filtrate from the gold precipitate is evaporated to dryness, and the residue is gently heated to destroy the small quantity of hydroquinone. The platinum residue is dissolved in *aqua regia*, the solution is evaporated with sodium chloride and then three times with hydrochloric acid, and the platinum is precipitated from the aqueous solution by boiling with sodium formate. A number of other aromatic compounds including resorcinol, pyrogallol, phenylenediamine, pyrocatechol and phloroglucinol, were found to act like hydroquinone in quantitatively precipitating gold. W. R. S.

Determination of Zinc in Metallic Cadmium. J. J. Lurie and V. F. Neklyutina. (*Zavodskaya Laboratoriya*, 1936, 587–589.)—Ten g. of the cadmium are dissolved in 120 ml. of dilute (1:3) hydrochloric acid, the solution being completed by boiling and adding two portions of 1 to 1·5 ml. of nitric acid (sp.gr. 1·4). Four g. of aluminium foil or shavings are added, followed, after 2 minutes, by another 1 g. The flask is shaken and allowed to stand for 10 to 20 minutes, after which a final 1-gram portion of aluminium is introduced. The excess of aluminium (about 4 g.) and the separated cadmium are filtered off on cotton-wool, and washed with 2 per cent. hydrochloric acid, and the filtrate is evaporated with sulphuric acid. The residual cadmium is now removed as cadmium sulphide, and the zinc is determined with precautions which are described in detail in the article. S. P. S.

Determination of Zirconium in Steels with *n*-Propylarsonic Acid. H. H. Geist and G. C. Chandlee. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 169–170.)—The steel (3 g.) is dissolved in 40 ml. of strong hydrochloric acid, and sufficient nitric acid is added to oxidise the iron. The solution is evaporated to dryness, the residue is moistened with hydrochloric acid, and the evaporation is repeated. The dry residue is heated for half-an-hour at 105 to 110° C., cooled, and dissolved by gentle warming in 10 ml. of strong hydrochloric acid. The solution is diluted to 100 ml. and filtered while hot, and the residue is washed with hot water and ignited in platinum. The silica is driven off with hydrofluoric and sulphuric acids, the residue is fused with sodium carbonate, and the melt is extracted with hot water. The residue is collected, washed, ignited, and fused with bisulphate. The filtered solution of the melt is added to the original hydrochloric acid filtrate, and the liquid (300 ml.) is boiled and treated with 40 to 50 ml. of a 5 per cent. aqueous solution of *n*-propylarsonic acid. After half-an-hour's digestion the hot liquid is filtered, the zirconium precipitate is collected and washed with hot water, and the filter is returned to the beaker and disintegrated with hot hydrochloric acid (10 ml.). After dilution with 100 ml. of water, the zirconium is re-precipitated with 10 ml. of reagent. The precipitate is treated as before, ignited in a porcelain crucible over a Méker burner, and weighed as ZrO_2. If stannic oxide is present, it can be completely volatilised by heating with ammonium iodide to constant weight. Tin is partially precipitated by the reagent, but no other metals interfere, and it is unnecessary to peroxidise titanium as in the phosphate method. W. R. S.

Detection of Cerium. J. F. Miller. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 181–182.)—A 5 per cent. solution of sodium arsanilate produces a red-brown colour in ceric solutions. With traces of cerium, a pink colour is produced. Fluoride interferes with the reaction; zirconium salts give a white precipitate. Cobalt and chromium, by reason of their coloured solutions, obscure the reaction. Cerous salts, the other rare earths, and most common metals are without effect. The reaction should not be used for quantitative colorimetry, as the colour gradually fades in dilute solutions. W. R. S.

Separation of Uranium, Zirconium and Titanium from Manganese, Cobalt and Nickel by Pyridine. E. A. Ostroumow. (*Ann. Chim. anal.*, 1937, **19**, 89–93.)—The investigations described in two earlier papers (ANALYST, 1936, **61**, 723, 795) have been continued. *Zirconium.*—The chloride solution is neutralised with ammonia, a slight cloudiness is cleared with dilute hydrochloric acid, and the solution is treated with 3 g. of ammonium chloride or nitrate and heated to boiling. The liquid is stirred and treated with methyl red and 20 per cent. pyridine solution until the indicator turns yellow, after which 15 to 20 ml. of precipitant are added. The solution is digested for 30 to 40 minutes on a steam-bath, the precipitate coagulating. It is collected, washed with 3 per cent. ammonium nitrate solution containing a few drops of pyridine, and dried and ignited in a tared porcelain crucible over a blast-burner. Sulphates do not interfere with the precipitation, but the precipitate contains basic sulphate which must be decomposed by strong ignition to constant weight.

Titanium.—The neutralised solution, prepared as described above, becomes cloudy when heated, the titanium salt hydrolysing. If the precipitation is effected from a more acid medium, the indicator still shows acid reaction after addition of excess of precipitant, but the precipitation of the titanium is quantitative. The precipitate is washed and ignited as described under zirconium. *Separation from manganese, cobalt, and nickel.*—The acid chloride or nitrate solution is treated with 5 g. of ammonium salt per 100 ml., and neutralised as before. It is vigorously stirred, after being heated to 90° C., and treated drop by drop with the precipitant, which is added in excess (15 to 20 ml.). After the precipitate has settled on a steam-bath, the solution should show a yellow tint, otherwise more pyridine is required. Preliminary neutralisation of the solution must always be carried out by means of ammonia. The separation is practically quantitative in one operation. A chloride solution is to be preferred to one of sulphate in presence of uranium. The sum of titania, zirconia, and uranic oxide in the solution should not exceed 0·1 g. W. R. S.

Iodimetric Determination of Sulphide in Cyanide Solutions. W. D. Djatschkow and L. P. Sajzewa. (*Z. anal. Chem.*, 1937, **108**, 326–328.)—The procedure consisting in the addition of the solution to be tested to a measured excess of acidified 0·1 *N* iodine solution, and titration of the excess of iodine with 0·1 *N* thiosulphate solution, was found to be unaffected by the presence of cyanide. The authors use 20 ml. of iodine solution acidified with 20 ml. of hydrochloric acid (1:4). W. R. S.

Volumetric Determination of Sulphate with Barium Chloride and Sodium Rhodizonate. A. Mutschin and R. Pollak. (*Z. anal. Chem.*, 1937, **108**, 309–316.)—The procedure indicated in the first communication (ANALYST. 1937, 331) is given in detail. The standard is a 0·2 *N* solution of ammonium sulphate prepared by neutralisation of sulphuric acid (methyl red indicator) standardised against pure potassium bicarbonate. The 0·2 *N* barium chloride solution used is standardised against the ammonium sulphate solution under the same conditions as the assay. The indicator is a freshly-prepared saturated solution of sodium rhodizonate. It decomposes after 3 to 4 hours. If the gravimetrically determined titre of the barium solution is taken as the standard, a negative error of the order of 1·5 per cent. is incurred.

The sulphate solution (50 ml.) is exactly neutralised to methyl red with hydrochloric acid or ammonia, and treated with ammonium chloride (2 per cent.) and acetone (35 per cent. by volume). The barium solution is added in portions of 2 to 3 ml., the flask being briskly shaken during the whole of the titration, and a drop of indicator is added after each addition of barium solution. When the indicator turns red, showing excess of barium chloride, the flask is shaken and left for a minute. More indicator is added (1 to 1·5 ml.), which produces a bluish-red colour if the excess of barium solution is sufficient (about 2 ml.). The excess is next ascertained with standard ammonium sulphate solution, added at the rate of 2 drops with intervening agitation of a few seconds. Shortly before the end-point the tint shades into orange. The sulphate solution is now added slowly, one drop at a time with vigorous shaking. The end-point is a colour change from orange to pale yellow.

In presence of 1 to 2 per cent. of sodium chloride satisfactory results were obtained with a titre determined as above under identical conditions, but 1 per cent. of potassium chloride caused some retardation in the end-point. Magnesium chloride (1 to 2 per cent.) acted like sodium chloride. As calcium sulphate is sparingly soluble in the acetonic medium, the authors advise addition of the prescribed quantity of acetone after the treatment with excess of barium solution and slow, dropwise addition of the sulphate solution, with thorough agitation. Considerable quantities of lime retard the reaction materially. The method was applied to a potable water, one litre of which was concentrated to 50 ml. after neutralisation to methyl red. Zinc and cadmium require a larger excess of barium solution (*i.e.* 6 to 8 instead of 2 to 3 ml.), otherwise the procedure remains the same. Ferric iron must be removed in the usual manner by precipitation with ammonia, the filtrate being concentrated to 50 ml. by evaporation. Aluminium and phosphoric acid interfere in the volumetric method; nitrates should be destroyed by the customary evaporation with hydrochloric acid. The sulphate concentration should not exceed 0·2 g. of SO_4 per 100 ml. The maximum volume of the liquid under treatment is given as 150 to 170 ml., with 35 per cent. of acetone and 2 per cent. of ammonium chloride. W. R. S.

Determination of Sulphide Sulphur in Portland Cement. H. A. Bright. (*Bureau of Standards J. Research*, 1937, **18**, 137–139.)—A modification of the usual evolution method is employed in which stannous chloride is used during the solution of the sample to prevent oxidation of the hydrogen sulphide by higher oxides of manganese and iron. A 5-g. sample of the cement is placed in a flask fitted with a ground-glass stopper carrying a thistle-funnel reaching nearly to the bottom of the flask and a leading tube, embodying a splash-bulb, bent down at right angles and dipping into an absorbing solution (285 ml. of water and 15 ml. of an ammoniacal zinc sulphate solution made from 50 g. of zinc sulphate crystals, 150 ml. of water and 350 ml. of ammonia, sp.gr. 0·90) contained in a beaker. Ten ml. of water are added to wet the cement thoroughly, followed by 25 ml. of stannous chloride solution (10 per cent.) and 65 ml. of dilute hydrochloric acid "(10 + 3)." The contents of the flask are boiled gently for 6 minutes, a slow stream of air being passed through the apparatus during the heating and for 3 or 4 minutes after the heating has been stopped. To the absorbing liquid is added a little starch indicator and 40 ml. of dilute hydrochloric acid (1 + 1). The liquid is immediately titrated with standard potassium iodate solution (0·03 *N*; 1·12 g. of potassium iodate and 12 g. of potassium iodide per litre) until a permanent blue colour is obtained. A blank test with the reagents mentioned above is advised. The potassium iodate solution is standardised against 0·03 *N* potassium permanganate solution as follows:—To 300 ml. of water are added 10 ml. of conc. hydrochloric acid and 1 g. of potassium iodide; after cooling, 25 ml. of the standard permanganate solution are added, and, after 5 minutes, the liberated iodine is titrated with thiosulphate solution (approximately 0·03 *N*), starch being used as indicator. This procedure is repeated, except that 25 ml. of the potassium iodate solution are substituted for the potassium permanganate solution; the normality of the iodate solution is then found by dividing the volume of thiosulphate solution required in the second titration by the volume required in the first, and multiplying by the normality factor of the permanganate solution; 1 ml. of *N* potassium permanganate = 0·01603 g. of sulphur. S. G. C.

Analysis of Portland Cement. T. Mizuno. (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 55B.)—It is claimed that a slight modification of the usual process, consisting in the addition of solid ammonium chloride to the liquid after decomposition of the sample with hydrochloric acid and previous to evaporation to dryness, leads to a more quantitative recovery of silica. S. G. C.

Preparation of the Acid Salt $3(NH_4)_2SO_4,H_2SO_4$ [Triammonium hydrogen disulphate]. P. Laffitte and P. Locuty. (*Ann. Chim. anal.*, 1937, **19**, 61–63.)—The acid salt $3(NH_4)_2SO_4,H_2SO_4$ provides a convenient means of preparing a standard acid solution by direct weighing. The following improved method of preparation was based on a study of the ternary system $(NH_4)_2SO_4$–H_2SO_4–H_2O, and depends essentially on the authors' finding that the salt crystallises in a pure state from aqueous solution at 0° C. A mixture of neutral ammonium sulphate (875 g.), conc. sulphuric acid (175 ml.) and water (325 ml.) (the proportions corresponding with the formula of the acid salt) is heated to boiling until the ammonium sulphate is completely dissolved, a little more water being added if necessary. The solution is cooled to 0° C., with vigorous shaking to produce small crystals, which are filtered off on a Buchner funnel (also cooled to 0° C.) and washed six or seven times with ice-water. It is preferable to use the minimum amount of water in washing. The crystals are finally dried *in vacuo* over sulphuric acid. The salt was found to contain H_2SO_4, 19·71 per cent.; $(NH_4)_2SO_4$, 80·10 per cent. (theory 19·83 and 80·17 per cent., respectively). It was not appreciably hygroscopic in moderately dry air. The salt prepared according to the method of Dunnicliff (*J. Chem. Soc.*, 1923, **123**, 476) was found to be slightly too acid, containing 20·19 per cent. of H_2SO_4. S. G. C.

Microchemical

Colour Reaction of Copper with Urobilin. G. Bertrand and L. de Saint-Rat. (*Microchemica Acta*, 1937, **1**, 4–8.)—A 0.1 per cent. alcoholic solution of urobilin is a very sensitive and specific reagent for copper, especially in neutral solution. Acid solutions should be nearly neutralised and then buffered with a little sodium acetate. Alcohol reduces the interference of hydrogen ions, and the test is best carried out in a medium in which the ratio of water to alcohol is about 50:100. The following metals do not interfere when present in 10 times the concentration of the copper (0·01 mg. Cu per ml.):—aluminium, barium, calcium, cadmium, cobalt, iron, magnesium, manganese, nickel, strontium and zinc. Ferrous iron does not colour urobilin itself, but intensifies the copper colour. Zinc gives a slight fluorescence which does not interfere with the copper colour. The reaction colour is pink at a dilution of 1 in 1,000,000, and turns to purple at a dilution of 1:100,000. Alternatively, copper salts may be used to detect urobilin.

J. W. M.

Quantitative Determination of Small Amounts of Cadmium with Dithizone. H. Fischer and G. Leopoldi. (*Microchemica Acta*, 1937, **1**, 30–42.)—Cadmium may be determined colorimetrically by means of a solution of 4 mg. of purified dithizone in 100 ml. of pure carbon tetrachloride or chloroform. The test solution, which must be nearly neutral, should contain about 3 to 40γ of cadmium in 5 to 10 ml.; more than 40γ must not be present, as the solubility of the complex in carbon tetrachloride is small. An equal volume of 10 per cent. sodium hydroxide is added, and the coloured compound is extracted with carbon tetrachloride in a separating funnel. Cadmium may be determined in this way in the presence of all the other elements except copper, silver, gold, mercury, palladium, nickel and cobalt; when silver and mercury are present the cadmium is first extracted with chloroform as the pyridine-thiocyanate complex; copper, if present, must be reduced to the cuprous state before the extraction of the cadmium. In the presence of zinc, cadmium is first precipitated as cadmium sulphide. Tin, if present, must be eliminated by evaporating the solution to dryness with a mixture of bromine and hydrobromic acid. J. W. M.

Fluorescence Analysis. The Thalleioquin Reaction. M. Haitinger. (*Microchemica Acta*, 1937, **1**, 1–4.)—Eosin and fluorescein can be detected in solution in a concentration of 10^{-10} and 10^{-14}, the amount being 10^{-7} to $10^{-11}\gamma$, which is far less than the usual range of micro-analysis. When there is a change of colour-tone at a certain concentration this may be applied in a quantitative estimate of the substance. The fluorescent aluminium and beryllium salts of morin are utilised as sensitive tests for these metals. Among other examples is the reaction given by quinine, bromine water and ammonia (thalleioquin reaction), the green colour of which is appreciable by daylight in a concentration of 1:20,000 of quinine, while by the use of ultra-violet light the fluorescence under suitable conditions is appreciable in a dilution of 1:500,000. A drop (0·05 ml.) of the test solution is placed on filter-paper and held while moist in bromine vapour. At first there is a brightening of the fluorescence, followed by extinction. At the beginning of the extinction the paper is held over an ammonia bottle; this causes the fluorescence, as viewed in ultra-violet light, to change suddenly from blue to greenish-yellow. The limit of identification is 0·4γ of quinine. The method is suitable for the detection of quinine in urine. J. W. M.

Periodical:—***Microchemica Acta.*** Published by Springer, Vienna. Vol. I, No. 1, 1937. Price 36RM. per volume (3 numbers).—The rapid development of micro-chemistry has stimulated the production of a new journal of micro-chemistry, covering all its aspects: analytical, preparative, physical, inorganic, organic, biological and technical, including what is termed semi-micro-chemistry. Original articles are printed in German, English or French; every article includes a short summary written in all the three languages. The first issue contains 15 original articles, one "Sammelreferat" on a biological subject, and 14 pages of references to recent papers on micro-chemical subjects. Of the 15 papers, 3 are written in English and 2 in French. Abstracts of suitable papers will appear in this journal.

J. W. M.

Reviews

ANNUAL REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY. Vol. XXI for 1936. Issued by the Society of Chemical Industry. Pp. 869. Price to members, 7s. 6d.; to non-members, 12s. 6d.

Since the present reviewer commented on the volume for the year 1929 (ANALYST, 1930, **55**, 532), this report has been enlarged by over one hundred pages, and has become an increasingly valuable record of recent progress in the many sections of industrial chemistry with which it deals. The present report is a comprehensive one, and the chemist who wishes to keep himself informed of the main work done in his own and related branches of applied chemistry cannot do better than consult it. Indeed, in these times when all chemists spend somewhat laborious days, one can scarcely follow the trend of industrial research without the help which a full résumé of this kind puts at one's disposal.

Nearly 900 pages in length, with adequate indexes occupying 74 pages, the 1936 report worthily takes its place besides its predecessors as a most timely record of the advances made in all the important branches of industrial chemistry. The Editor (Mr. T. F. Burton) is to be congratulated on the imposing list of authoritative writers to whom the various chapters of this work have been entrusted; the names themselves are a guarantee of the accuracy and soundness of the 26 articles constituting the volume. The sections on "Oils and Fats," "Soils and Fertilisers," "Sugars and Starches," "Fermentation Industries," "Foods," "Fine Chemicals," and "Sanitation and Water Purification" are of special value to readers of THE ANALYST; but all the chapters are of general interest, and will be found indispensable to those concerned with particular aspects of our science in its everyday applications.

Little new remains to be said concerning these reports, for they have received frequent notices in this journal, and they continue to maintain their high literary and scientific standard. Many of the chapters contain important critical comments on the work reviewed, a most valuable feature. The references are commendably up-to-date, and a full bibliography of all the papers cited is given in the footnotes. In many sections details of analytical procedure are provided. There are informative articles on liquid and solid fuels, atmospheric pollution, low-temperature carbonisation of coals, plasticisers, synthetic resins and rubber, glass, metals, corrosion, water softening and conditioning, and road-tar specifications.

The volume is well produced, and is notably free from typographical errors. The reviewer notices that the important subject of vitamins is dealt with from varying aspects, in at least four separate sections of the volume, by different writers, and it might be well to consider in the future whether it would not be worth while, in order to obtain a comprehensive view, to have one single article on this subject.

Previous reviews of these reports in THE ANALYST, including one by the present writer, have pointed out the desirability of giving the reader some explanatory notes on the abbreviated name references to the journals cited, but one still looks in vain for a page devoted to them. ARNOLD R. TANKARD

OFFICIAL AND TENTATIVE METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Fourth Edition. Pp. xx + 710. Association of Official Agricultural Chemists, Washington, D.C. 1935. Price $ 5·50 net.

The Methods of Analysis of the A.O.A.C. are so well known to the majority of food and agricultural chemists in this country that it is quite unnecessary to describe their general scope. Since the first issue British chemists have used these methods on many occasions when it might be desirable to cite a recognised and official method. The ground covered is much wider than the name of the issuing body would appear to imply; but anyone having the slightest acquaintance with the Association or with its Journal or with previous editions of the Methods is more likely to expect too much than too little.

The need for official methods is felt most strongly when there exists some legal or other analytical standard for articles. In the United States there are a number of standards for food and agricultural products, and the methods of the A.O.A.C. are used in their enforcement. In this country there are few such standards, and the need for official methods has been largely met by certain Statutory Regulations, such as the Fertilisers and Feeding Stuffs Regulations; by methods published under the auspices of the Analytical Methods Committee of this Society; and by certain specifications and methods, such as those drawn up by the Association of British Insecticide Manufacturers and the British Standards Institution. Occasionally, methods become the equivalent of official methods by common consent, as, for example, Monier Williams's method for sulphur dioxide. But we have no one volume in which a large number of methods are collected and issued by some recognised authority. If any legislative action is taken in this country in respect of general food standards, the Council of this Society may well be faced with the decision as to whether or not it is necessary to issue a comprehensive compilation of methods of analysis. If the decision were in the affirmative, the volume under review would undoubtedly be taken as a guide for a first draft.

The policy of the Association is to issue a new edition of its Methods every five years, but copies are not available for some little time after their nominal date of publication. Each new edition is opened by chemists in this country with considerable interest, in particular to see what new matter has been added. One can be sure that the standard material will be substantially unaltered; that certain tentative methods in earlier editions will be improved; occasionally methods are removed. In the latter event it may be that a general method has been elaborated, rendering several particular methods redundant; or that temporary interest in a subject has so waned that its treatment is no longer deemed necessary. Rarely, and so rarely that it deserves mention, is a method deleted because it is unsatisfactory. The new material always repays study because here are methods produced by a team of collaborative workers who regard them, after exhaustive trial, as the best for the purpose at the time of issue.

As an indication of the growth of this publication it may be mentioned that the three previous editions dated 1920, 1925 and 1930 had, respectively, 417, 535 and 593 pages. The present edition, dated 1935, has 710. The deletions include the unsatisfactory method for fluorine in baking powder and the complicated Heidenhain's method for the determination of carbon dioxide. A general method for the determination of lead has involved deletion of several methods applied to specific substances. Revision of some of the methods and improvement of certain diagrams are welcomed. Apparent specific gravities are now determined at

$$\frac{t^\circ\ \text{C.}}{t^\circ\ \text{C.}}\ \text{instead of}\ \frac{t^\circ\ \text{C.}}{4^\circ\ \text{C.}}$$

Of the new material, the most interesting is probably that dealing with selenium. The poisoning of stock by selenium has recently become an important problem in America, and has occasioned some interest in this country. The inclusion of methods for its determination in soil and in plants is therefore timely.

Of late years considerable attention has been paid to, and concern has been felt regarding the resulting effect on soil of the continued use of, artificial fertilisers, and the added methods for determining the acid-forming or non-acid-forming qualities of fertilisers are valuable in this connection.

The scope of the work on the examination of plants has been extended by methods for the determination of iodine and of lignin. General methods are included for nut products, and particular methods for peanut butter, almond paste and shredded coconut. Other new matter includes the phenol coefficient of disinfectants (the method of the U.S. Food and Drug Administration, which is analogous to the Rideal-Walker test), the examination of oleo-resinous varnishes, the examination of malt, and Nyns's method for laevulose. Methods are added for methyl alcohol (as tetramethyl ammonium iodide) in distilled liquors, lactose in milk chocolate and process cheese, benzoyl peroxide in flour, gums in cheese, glycerol in egg products, malic acid (both laevo- and inactive) in fruit products and iodine in mixed feeds. A biological assay of vitamin *D* in grain and stock feeds is given, and the method of the American Public Health Association has been adopted for dirt in milk. The general methods for lead occupy 18 pages, all possibilities being apparently provided for; the various processes include modifications involving sulphide precipitation, dithizone extraction, electrolytic separation, removal of tin and bismuth by volatilisation and extraction respectively, and final determination of lead colorimetrically, iodimetrically or photometrically. The number of alkaloids for which microchemical tests are given has been doubled, and a similar series of tests is given for a number of "synthetics."

Two of the reference tables deserve special mention because of their usefulness. The alcohol table is greatly extended by giving the complete range of percentage of alcohol by volume at 60° F., corresponding to apparent specific gravity at $\frac{t^\circ\ \text{C.}}{t^\circ\ \text{C.}}$, where t is 15·56, 20, 22, 24, 25, 26, 28, 30, 32, 34, 35, and 36. The table correlating Zeiss immersion refractometer readings with alcoholic strength covers 9 temperatures between 17·5° C. and 25° C.

Practising chemists in food and agricultural products have long realised that the first place to look for satisfactory methods to be used in the examination of something not in their current work is this publication. Nor, if the subject is dealt with, are they disappointed. One could mention several determinations within the general scope and worthy of a place, which are not included; but it would be unjust to criticise the book on this account. It is not only a question of covering certain chosen ground, but also of surveying each piece of that ground by a team of workers who are only human and cannot deal with all aspects at once or at the same rate. Anyone who has been concerned with collaborative work will know how difficult it is in certain cases to arrive at the point when all the workers are satisfied.

As usual, the work is well printed and produced, only a very few unimportant misprints having been noted. Familiarity leads one to disregard the numerous abbreviations and American spellings. Occasionally, expressions not usually associated with scientific methods are employed; but what could be simpler or more descriptive than the instructions in the treatment of fruit parings which involve stewing to produce a mush without stringiness?

There can be but one opinion of this book, that it is the best edition so far issued and that it is indispensable to the food and agricultural chemist.

J. R. NICHOLLS

A TEXT-BOOK OF INORGANIC CHEMISTRY. Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Vol. VI, Part V, ANTIMONY AND BISMUTH. W. E. THORNEYCROFT, B.Sc. Pp. xxviii + 249. London: Charles Griffin & Co., Ltd. Price 18s.

The main impression one brings away from this book is one of vast numbers of original references; every one of its 222 pages of text contains footnotes, averaging probably about 8 to a page; almost every footnote contains at least one reference, many contain 10 or upwards. This in itself is a very excellent feature and one which can hardly be overdone; whether, however, all these multitudinous references have been read with discrimination is another matter; it would probably be too much to ask of human nature that they should have been. Such few as were consulted lent point to this suspicion; one on page 117 (B. S. Evans, ANALYST, 1932, 554) ascribes to that author a statement he certainly did not intend; one on page 155 gives one of Mr. Pope's bibliographies in THE ANALYST as a reference for "the physiological action of bismuth"; again, on page 162 occur the two apparently contradictory statements drawn from two references, "it ($BiCl_3$) will dissolve to a slight extent in liquid hydrogen sulphide," and "$BiCl_3$ reacts immediately with liquid hydrogen sulphide, even at low temperatures, forming . . . $BiSClBiCl_3$." The author certainly cannot prevent writers of papers contradicting each other, but he ought not to give both statements, separated by a considerable amount of intervening matter, without comment.

The book is approximately equally divided between antimony and bismuth, and is prefaced by a list of abbreviations and by the table of dates of issue of journals, which appears to be common to all the volumes of this series. In view of the severe condensation and the fact that at least some of the reactions of the two metals (for example, the reduction of their salts to metal by sodium hydrosulphite) have been omitted, it is questionable whether certain of the sections, such as those dealing with metallurgy and with the existence of a number of hydrates (some of them exceedingly dubious), might not profitably have been curtailed. In describing reactions the all-important question of physical state is frequently omitted, and there is a lack of working detail throughout the book. This is excusable where space is a consideration, but only so when economy of that space has been observed; also, it is irritating to be given a relatively long section dealing with the preparation of some substance (hydrate, for example) immediately after being told that that substance probably does not exist at all.

It is strange, in a book dealing with the chemistry (including the analytical chemistry) of antimony, to find no mention of the name of Reinsch. His name is mentioned once in the section on bismuth, and that in support of a statement which is not true, namely, that bismuth is only partially precipitated by copper. The Reinsch reaction for antimony is ascribed to two Italian chemists in 1925, and a French one in 1930, and then only as a means of preparing the violet compound Cu_2Sb; also it is stated that cuprous chloride must be added, which is not by any means necessary.

In spite of failings, however, the book is a valuable addition to Dr. Newton Friend's text-book. The author has cast his net very wide indeed, and the vast number of references enables the reader to go at once to the original sources of the information. It is produced in Messrs. Griffins' familiar style, and the printing is excellent; in fact, no printing errors or proof-reading slips were noticed, unless mention of "a solution of bismuth nitrate in mannitol and sodium thiosulphate" may be counted as one.

B. S. EVANS

PHYSIOLOGY FOR PHARMACEUTICAL STUDENTS. By H. H. BARBER, B.Sc., Ph.D., F.I.C. Pp. 477, 131 figures. London: Baillière, Tindall & Cox. 1937. Price 12s. 6d.

Physiology has recently been introduced into the course for the pharmaceutical qualifying examinations, and this book has been written for pharmaceutical students. The introduction of a new subject into a curriculum is always interesting, for it may alter the trend very considerably if the subject is so much alive as is physiology to-day. The first text-book for the students' use, therefore, excites some curiosity.

The book has 464 pages of text; this is too large. Teachers seem unable to look at their subject from the students' point of view. Big text-books, and lectures filled with detail, result in a burden on the student, and when a subject becomes burdensome, little is remembered after the examination is over. A book of half the size would have been of more value.

The chemical part is on the whole well written and interesting; but to this there are exceptions, as, for example, the section on the transport of carbon dioxide in the blood. It is to be hoped that the students are amazed when they read that "when arterial blood takes up carbon dioxide from the tissues, the carbonic acid combines with the sodium chloride in the plasma to produce more bicarbonate." They may well ask "What sort of chemistry is this?"

The physiology proper in the book is scarcely there. Physiology is always fascinating—a story full of the most ingenious devices, but of this the reader gets no impression. The author has prepared the book with much labour, but the writing remains dull, because he has depended so largely on existing text-books of physiology which contain much that is neither interesting nor important, and he has not selected well.

For the pharmaceutical student a fairly thorough study of the glands of internal secretion is required, both for the Chemist and Druggist and for the Pharmaceutical Chemist qualification. The treatment of this subject in the book is so scanty as scarcely to be worth calling a treatment at all; it occupies 25 pages. A similar number of pages is allotted to the pharmacology "of some typical substances"; in this chapter again the information consists of a series of statements, which are not explained or amplified. There are also 16 pages on vitamins.

The book contains a series of practical exercises at the end of many of the chapters.

J. H. BURN

THE METABOLISM OF LIVING TISSUES. By ERIC HOLMES, M.A., M.D. Pp. xii+236. Cambridge University Press. 1937. Price 7s. 6d.

Dr. Holmes, according to his own preface, set himself the object of considering "the metabolic activity of various tissues—the liver, the kidney and so forth—rather than to follow the chemical changes suffered, for instance, by a protein molecule during the course of metabolism." His justification for this perhaps somewhat iconoclastic innovation is that the dynamic aspect of tissue metabolism will be thereby made more apparent.

Actually his book, in its working out, proves to be a compromise between the proposed and the discarded method—and a very good compromise too. It is to be regarded primarily as an exposition of tissue enzyme cycles, in so far as the experimental method has been able to elucidate the chemistry of the enzymes and the physiology of the cycles. Like all expositions of a changing and growing branch of science by one working in it, it is full of interest and stimulant of speculation. Particularly fascinating is Dr. Holmes's account of the alternative routes for carbohydrate oxidation, with an explanation of the rôles attributed to lactoflavin, adenylic acid, creatine and the various phosphoric esters.

There are signs that this book was written with increasing haste as it progressed, and unfortunately this autocatalytic process has brought with it some curious phraseology, some inadequate proof-reading and some inaccuracies of fact in the later section. Surely the statement, "Exactly how these two hormones exert their action is still a matter for experiment," is so deficient in the logic of grammar that an M.A. of Cambridge University can only have passed it in excess of speed. Vitamin B_2, again, is *not* the anti-pellagra factor, and is *not* believed to be a flavin derivative; a part of this complex is *certainly* a flavin and that part is certainly *not* pellagra-preventing. Statements about the presence of carotene in liver oils and the chemistry of its conversion to vitamin A have been simplified to the point of inaccuracy. Further, the classical "irradiated sawdust" experiments at the Lister Institute have been re-interpreted in the light of subsequent knowledge in such a way as to present an historically misleading picture.

Finally, apart from printers' errors, of which there are several, there is some inconsistency in the ways of presenting the same formulae or molecular groupings in different parts of the book, and this might well confuse non-chemical students, for whom, as well as for chemists, this book is otherwise a store of interesting and important information. This fact should be, perhaps, reiterated and stressed, for the reviewer has felt obliged in the last paragraph to play a somewhat critical Mr. Watson to Dr. Holmes, and he must therefore insist that any errors in the book are, on account of its all-round scope, co-ordinating outlook and wide knowledge, very well worth correcting. When this has been done, it will become a worthy companion to another book in the same series, reviewed recently in THE ANALYST (1937, **62**, 239). A. L. BACHARACH

PRACTICAL EVERYDAY CHEMISTRY. Edited by H. BENNETT. Pp. 305. London: E. & F. N. Spon. 1936. Price $2.

This is in effect a cheaper edition of the chemical formulary—a chemical "cook book." The recipes range from brushless shaving cream to potato blight control; from Gorgonzola cheese to ant-poison; from stiffeners for toes of shoes to cherry brandy; from pineapple icing to wax crayons; from concrete floor hardeners to photographic intensifiers; and include three methods for the removal of tattoo marks. A couple of examples may be quoted:

Cockroaches, exterminant for.—Powdered borax, 4; flour, 2; chocolate powder, 1; parts by weight.

Anti-rust varnish.—Coumarone China-wood varnish, 25; white spirit, 15; lead chromate, $\frac{1}{4}$ parts.

The book is extremely comprehensive, but, whilst the composition of the products is given, the working details are often too brief, or are altogether omitted. Thus, such important factors as temperature of mixing, rate of cooling, time of heating, and engineering details of vital importance in the manufacture of high-grade products, are hardly dealt with at all.

The book makes very interesting light reading for the chemist who enjoys manufacturing products such as floor polishes, face cream or scouring soaps in the home, and for all who want to know "what is it made of?" A very useful list of manufacturers from whom the necessary ingredients of the recipes may be bought is given at the end of the book; unfortunately for readers in this country all the addresses are in the United States of America. JANET W. MATTHEWS

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Honours

The President and Council of the Society have congratulated the following members on the Honours conferred upon them on the occasion of His Majesty's Coronation:

Dr. Robert Howson Pickard, F.R.S., *President of the Institute of Chemistry*—Knight Bachelor.

Lt.-Col. Clive Newcomb, M.D., F.I.C.—Companion of the Most Eminent Order of the Indian Empire (C.I.E.).

Mr. Andrew More, F.I.C., *Deputy Government Chemist*—Companion of the Imperial Service Order (I.S.O.).

Sir Robert Pickard has also been congratulated on his appointment as Vice-Chancellor of the University of London.

NORTH OF ENGLAND SECTION

The Eighth Summer Meeting was held at the Prince of Wales Hotel, Scarborough, from June 4th to 7th. There was an attendance of sixty, including many ladies.

The Chairman (Mr. Arnold R. Tankard) presided, and among those present were the following:—President (Dr. G. Roche Lynch); Past-Presidents (Dr. B. Dyer with Mrs. Dyer, Dr. J. T. Dunn with Mrs. Dunn, Mr. E. R. Bolton and Mr. J. Evans); Hon. Secretary (Mr. L. Eynon); Editor of The Analyst (Dr. C. A. Mitchell); Chairman of the Scottish Section (Dr. J. F. Tocher), Hon. Secretary (Mr. J. B. McKean); Mr. E. M. Hawkins, Dr. H. E. Cox and Miss Bradford.

The Chairman extended a cordial welcome to all present, especially those from the South and from Scotland. Dr. Dyer responded for the members from the South and Dr. Tocher for the Scottish members.

On Saturday morning Dr. J. J. Fox, O.B.E., F.I.C., Government Chemist, gave an address entitled, "The Functions and Usefulness of Analytical Chemists." Prof. T. P. Hilditch took part in the ensuing discussion. A vote of thanks to Dr. Fox for his address, moved by Dr. Roche Lynch and seconded by Dr. Dunn, was carried unanimously.

A resolution was unanimously passed expressing the greetings and affirming the loyalty of the Section to the Parent Society; it was proposed by Prof. W. H. Roberts and seconded by Mr. J. G. Sherratt.

Telegrams of greeting were received from Mrs. Chaston Chapman, Miss Elliott and Dr. E. B. Hughes.

The President expressed the regret of the members at the absence of Mrs. Tankard through illness.

Dr. Dyer conveyed the thanks of the meeting to the Honorary Secretary (Mr. J. R. Stubbs) for arranging the meeting. The help of the following members in carrying out the arrangements is gratefully acknowledged:—Mr. W. G. Carey, Mr. W. F. Elvidge, Mr. T. W. Lovatt, Mr. C. R. Louden and Mr. F. J. Smith.

On Sunday afternoon the party proceeded by motor over the moors to Whitby, where afternoon tea was taken.

The following is an outline of Dr. Fox's address:

Analytical Chemistry

By J. J. Fox, O.B.E., D.Sc., F.I.C.

Dr. Fox reminded his audience that this country lagged behind America and the Continent in the absence of a chair of analytical chemistry. The reason for this was not clear, unless it were due to a want of appreciation of the scope and purpose of analytical chemistry, which, after all, was an important part of the foundation of practical chemistry. He pointed to the work published in the established journals of analytical chemistry and asserted that it was of the same quality as that arising from other branches of chemistry.

Analytical laboratories were continually engaged in investigations, as the published work indicated. The application and extension of the methods of physical and general chemistry to analytical purposes was illustrated by various examples in actual use in industrial and other laboratories. The speaker indicated the necessity for the analyst to keep in touch with advances in other branches of chemistry, and also pointed out that most practising analysts were, in their own spheres, specialists in some branch of chemical knowledge. It was well-known to most of the audience that the analyst was continually in the position of having to realise the necessity of examining the basis of his operations. He was rarely able to accept, without examination, the methods he found described. This meant a large diversion of his activities in the direction of general investigation, unless he was content to remain dormant in his methods.

Whenever a little spare time became available, it was an amusing pastime to select a paper from The Analyst or one of the other journals of a similar character, put in a mathematical expression or two, and see how far the paper, so revised, met the requirements of "pure" chemistry; it was likewise instructive.

Obituary

LAWRENCE JOHN DE WHALLEY

By the death of Lawrence John de Whalley, on January 9th, 1937, our Society loses one of its oldest members.

De Whalley was born in 1853 in Lancashire, and received his early education there. In 1874 he won a Royal Exhibition at the Royal School of Mines, London, and for the next three years was a student at the School, where he attended the lectures of Frankland, Guthrie and Huxley, and was trained in practical chemistry by Valentin. In 1877 he took his B.Sc. degree at the University of London, and in 1879 became honorary assistant to Frankland at the Royal School of Chemistry (into which the Royal School of Mines had by then developed). About the same time he was also appointed lecturer on chemistry at Whitgift School, Croydon, and for many years he continued to be associated with that school as examiner in chemistry.

In 1889 de Whalley turned from the teaching to the industrial side of chemistry, and became chief chemist at the tar works of Messrs. Forbes, Abbot and Lennard at East Greenwich. While there he devised what afterwards developed into the first continuous still. This historic piece of apparatus, the precursor of many oil stills of its type all over the world, is not only in existence but is still working.

In the following year de Whalley succeeded his brother-in-law, the late John Joseph Eastick, as chief chemist to Messrs. Abram Lyle & Sons, later incorporated with Messrs. Tate & Lyle, Ltd., sugar refiners, of Plaistow Wharf, Victoria Docks, London, and he remained with them for the rest of his professional life, until his retirement in 1930.

De Whalley was a great authority on sugar refining, and although most of his work was unpublished, he inaugurated and perfected many improvements in refinery processes and control. He was a pioneer in this country in the use of kieselguhr for sugar filtration, and was probably the first to associate microscopic structure of the diatoms with rate of filtration. He was responsible for the introduction of affination at Plaistow Wharf, and made many improvements in the manufacture of golden syrup.

He took part in international conferences on sugar analysis in this country and on the Continent, and was Chairman at the Conference of Sugar Chemists (the Raffinose Conference) in 1910, in Berlin, when he contributed some work on raffinose in beet sugars. During the Great War he was a representative at the Royal Commission on Sugar Supply. He attended the opening meeting of the recent International Commission for Uniform Methods of Sugar Analysis in August of last year.

He was elected a member of this Society in 1882, and regularly attended its meetings and dinners until a few years before his retirement.

He was an original member of the Society of Chemical Industry, and an abstractor for the sugar section of that Society's journal from 1896 to 1915. In 1911 he was elected a Fellow of the Institute of Chemistry, and he was for many years a Fellow of the Chemical Society. One of the founders of the Chemical

Club, he was a member of the first committee, and also took an interest in the founding of the Institution of Chemical Engineers.

De Whalley was a good mathematician and linguist and a lover of the classics, which he read in the original Latin and Greek. He spoke French, German, Russian and Polish, and was often engaged in the translation of technical works, even to within a week of his death.

In addition to his scientific work, de Whalley found time to interest himself in many other spheres, and may be remembered by some as Honorary Secretary for many years, and later President, of the Cheerybles Musical Society. Freemasonry occupied some of his time, and he held high rank in the Grand Lodge of England.

From early boyhood until his death he was a student. His country upbringing, with biological training under Huxley and geological excursions with Seeley, had made him an ardent nature-lover. His many interests, the clear way in which he expressed his thoughts, and his remarkable memory, made him a most entertaining companion.

A quiet, modest, lovable man of unassuming manner, he was liked and admired by all who knew him. He was at all times ready with kindly help and advice for those who sought it.

De Whalley married, in 1883, the only daughter of Z. Eastick, an early gas-works chemist, and leaves a widow and twelve sons and daughters, nine of whom are married, and nineteen grandchildren. He will be sadly missed by his many friends.

H. C. S. DE WHALLEY

Quantitative Microscopical Analysis of Feeding-stuffs

I. Determination of Rye, Wheat and Barley Starches in Mixtures. "Ground Oats" Mixtures.

BY J. G. A. GRIFFITHS, B.A., PH.D., A.I.C.

(*Read at the Meeting, April 7, 1937*)

THE determination of the nature and the proportions by weight of the ingredients of an animal feeding-stuff sometimes involves the identification and determination of the proportions by weight of each of several products from the grains of different cereals. Chemical analysis usually affords only very general guidance, and recourse must be had to microscopy.

It is essential, before deciding upon a quantitative microscopical method, to identify the ingredients of a mixture, and the first part of this paper, which has particular reference to the adulteration of ground oats, is therefore concerned with the microscopical identification of products derived from the grain of oats, rye, wheat and barley, together with other starches which may be found in feeding-stuffs, and the presence of which may sometimes lead to confusion. In the second part of the paper (p. 513) the "lycopodium and starch grain" counting method has been extended, with the object of determining in mixtures the proportion by weight of each of two different ingredients of which the distinctive particles used in the counting process have closely similar characteristics, differing, perhaps, only in respect of the maximum size of the particles, *e.g.* the starches of wheat and barley. A detailed account is given of a means whereby it is possible to determine the respective proportions by weight of ground endosperm (flour) or comminuted whole grain of rye, wheat or barley in a feeding-stuff containing the starches of one or two of these cereals. Details are given, in Part II (p. 519), of a simple microscope projector technique of general application for the accurate counting and classification of particles according to size or other characteristics.

A. FACTORS CONTROLLING THE MICROSCOPICAL APPEARANCE OF CEREAL PRODUCTS

The following points concerning the microscopical examination of a mixture containing products derived from the grain of oats, rye, wheat and barley are relevant:

In the process of threshing, the husk is removed from wheat and rye so that the ground whole grain and products derived therefrom will contain material characteristic of the kernels only, that is, the bran and the contents of the grain. On the other hand, threshing does not remove the husk from oats and barley grain, so that the ground products of these cereals will contain material characteristic of the husk, bran and interior of the grain. Oat meal for human consumption is made by comminuting oats from which the husk has been removed, and such a product, which, if unfit for human consumption, may be used in animal feeding-stuffs, consists of bran particles and starch. The flours (ground endosperm) of wheat, rye, oats or barley, when unfit for human food or when very cheap, may be used in foods for animals. These flours consist of starch with only traces of bran tissue (including hairs). These traces, however, are of diagnostic value.

In principle, therefore, it is possible to determine whether a particular cereal ingredient of a mixture is a flour (ground endosperm) or a meal (comminuted whole grain) or a branny or husky by-product by determining the ratio of the weight of the characteristic bran fibre to that of the corresponding starch present.

Thus, if a sample of ground oats is found to contain lenticular starch of rye, wheat or barley, and if this starch is accompanied by only traces of tissue characteristic of the bran of these cereals, it is concluded that the cereal, which, incidentally, is identified by these traces, is present as flour. If, however, the cereal has been added in the form of a meal produced from the whole grain, the proportion of characteristic bran (and husk) tissue with respect to the corresponding starch will be correspondingly greater than with a flour. Similarly, an offal will show a greater proportion of bran or husk tissue, or both, than a meal made from the whole grain.

SOME DIAGNOSTIC FEATURES.—The microscopical appearance of cereal products is dealt with in detail in the standard works of Winton, Greenish, König, Moeller, and others. In general practice, the following features have been found to have the greatest diagnostic value:

OATS.

- (1) *Husk*:
  - (a) Occasional pieces with characteristic "*saw edge*" of closely packed short hairs.
  - (b) *Spongy parenchyma* of the flowering glume. Characteristic irregularly perforated appearance which differs from that of corresponding barley tissue.
- (2) *Bran*:
  - (a) *Geminate hairs* of epicarp.
  - (b) *Long hairs*. Tapering towards both ends (contrast with wheat).
- (3) *Starch*:
  - (a) Approximately *spheroidal aggregates*, about 40μ in diameter, distinguished from rye, wheat and barley starch grains by the faintly defined lines of demarcation between the angular grains and also by the evident differences in shape revealed on slowly rotating the aggregates under the microscope by gently moving (pressing on) the cover-slip with a needle.
  - (b) *Angular grains*. Less than 12μ in diameter. A few *spindle*-shaped and *dumb-bell*-shaped grains.

RYE.

- (1) *Bran*:
  - (a) *Cross cells of the pericarp*. Thick and characteristically "beaded" long walls and smooth unbeaded short walls (contrast with wheat).
  - (b) *Hairs*.
- (2) *Starch*: Lenticular, generally 25–50μ in diameter. Some grains have *stellate hila*. Many small grains, a few *hat* or *bell-shaped* (very rare in wheat). (*See also* p. 514.)

WHEAT.

- (1) *Bran*:
  - (a) *Cell walls* are often distinctly brown.
  - (b) *Cross cells of pericarp*. Thick and "*beaded*" walls (*cf.* rye).
  - (c) *Hairs*.
- (2) *Starch*: Lenticular, generally 25–40μ in diameter. Many small grains. (*See also* p. 514.)

BARLEY.

- (1) *Husk*: *Spongy parenchyma* of flowering glume. Cells have irregular, approximately rectangular outline. (*Cf.* Oats.)
- (2) *Bran*:
  - (a) *Aleurone layer*; 2 to 4 cells deep, thereby differing from other cereals. Cells about half the size of those of wheat and rye.
  - (b) *Cross cells of pericarp*. Thin, unbeaded walls, double layer.
  - (c) *Hairs*.
- (3) *Starch*: Lenticular, generally 20–30μ in diameter. Many small grains. (*See also* p. 514.)

OTHER STARCHES FOUND IN FEEDING-STUFFS.

(1) *Tapioca or Manihot starch* approximates to an irregular spherical form, generally truncated, less than 35μ in diameter, and may be confused with cereal lenticular starch. The latter, however, appears discoid when rotated under the microscope, and, further, each manihot starch grain shows, in contrast to rye, wheat and barley, a distinct cross when viewed by polarised light through crossed Nicols.

(2) *Ground-nut or pea-nut* starch is globular and less than 15μ in diameter.
(3) *Pea, bean, lentil.*
(4) *Sago, potato, arrowroot.*
(5) *Maize, dari* (sorghum), *rice, millet.*

In general, there will be found with these starches tissues of the parts of the plants from which the starches have been derived. For present purposes, further consideration of these starches has been omitted, but, when they are present, their characteristic features enable them to be identified, and analogous methods to those described later may be applied for determining their proportions by weight in the samples.

B. QUANTITATIVE MICROSCOPICAL ANALYSIS OF MIXTURES

Before undertaking a quantitative microscopical investigation of a sample it is essential to make a qualitative examination and to identify the ingredients.

BINARY MIXTURES.—The technique for determining microscopically the proportion by weight of one ingredient of a binary mixture has been described by Wallis,[1] and is outlined in the British Pharmaceutical Codex[2] (*see also* p. 519).

The following experiments with ground oats adulterated with wheat flour illustrate the application of the method to a feeding-stuff:—The sample (0·2000 g.) was mixed with 0·0400 g. of lycopodium, and 0·2000 g. of a standard mixture of ground oats and wheat flour (80 : 20 parts by weight) was mixed with 0·0400 g. of lycopodium. Appropriate counts (9 fields per slide) of the lycopodium spores and of the starch grains greater than 10μ in diameter were made, with the following results:

Sample mixture:

$$\text{Slide I.}\quad \frac{\text{Total wheat starch grains}}{\text{Total lycopodium spores}} = \frac{1263}{752} = 1{\cdot}68$$

Mean 1·655

$$\text{Slide II.}\quad \text{Ditto.}\quad \frac{482}{295} = 1{\cdot}63$$

Standard mixture:

$$\text{Slide I.}\quad \frac{\text{Total wheat starch grains}}{\text{Total lycopodium spores}} = \frac{1126}{578} = 1{\cdot}95$$

Mean 1·935

$$\text{Slide II.}\quad \text{Ditto.}\quad = \frac{673}{350} = 1{\cdot}92$$

$$\therefore\ \text{Wheaten flour in sample} = \frac{1{\cdot}655 \times 20}{1{\cdot}935} = 17 \text{ per cent. by weight.}$$

This method is also directly applicable to ground oats and other feeding-stuffs adulterated with rye flour or ground whole rye or with barley meal or, in general, with any single adulterant which has an ingredient of suitable particle size and can be recognised microscopically. The same method can be used to determine the composition of ternary, or other, mixtures only if each ingredient has particles with easily distinguishable characteristics.

TERNARY MIXTURES.—The method described above is not directly applicable to a ternary mixture containing rye and wheat or barley starches, for the following reason:—The characteristic (lenticular) starch grains of these three cereals approximate to the form of circular discs, and, although the average diameters of the starch grains are rye>wheat>barley, the following table shows that there is considerable overlapping, and therefore it is not possible to identify, by means of dimensions alone, an isolated starch grain in a mixture of these cereals unless the diameter exceeds the maximum for wheat.

	Diameter		
	Smallest μ	Average μ	Largest μ
Barley ..	2–7	20–30	40
Wheat ..	2–9	25–40	50
Rye ..	3–10	25–50	60

In the examination of these mixtures it is neither convenient nor necessary to deal with grains smaller than 10μ in diameter. A simple count, with respect to lycopodium, as described above, of the total number of starch grains greater than 10μ does not give a true measure of the percentage by weight of the total rye plus wheat or barley endosperm, or comminuted whole grain, in the sample, since the number of starch grains per unit weight of these products (generally) differs from cereal to cereal. The consequences of disregarding this point are illustrated later (p. 516). It is therefore necessary to determine the relative numbers of the starch grains of each cereal present.

GROUND OATS ADULTERATED WITH PRODUCTS FROM THE GRAIN OF RYE AND WHEAT OR BARLEY.—The ingredients of the mixture having been identified by the preliminary microscopical examination, it is necessary to decide which features of each particular ingredient are suitable for the quantitative work, it being assumed that such features have not been distorted or modified by heat or other treatment. In certain mixtures the starches are chosen as the basis of the determinations.

Rye starch differs from the starches of wheat and barley in two microscopical features of diagnostic value, *viz.* the hilum and the large size of a proportion of the grains.

(1) *The Hilum.*—Whereas the hilum of wheat and barley starch seldom appears larger than a small dot, centrally situated in the disc, the hilum of a small proportion of rye starch grains is stellate. In the samples of rye flour examined, the numerical proportion of starch grains, greater than 10μ in diameter, with stellate hila varied from 5 to 11 per cent. (average 7·5 per cent.) (see Table II).

(2) *Large Diameter of some Rye Starch Grains.*—Of the total number of starch grains of diameter greater than 10μ, in the samples of rye flour examined, 6·5 to 9 per cent. (average 7·5 per cent.) had a diameter greater than 40μ, whereas, in samples of wheat flour, less than about 1 in 300 of the total number of starch grains greater than 10μ in diameter exceeded 40μ in diameter. Barley starch grains do not exceed 40μ and seldom exceed 35μ in diameter (see Table III).

APPLICATION OF CRITERIA.—If, therefore, in a cereal meal containing lenticular starch grains there are found some starch grains with stellate hila, it is strong presumptive evidence that rye is present, and this is confirmed if there are lenticular grains of diameter greater than 50μ (*cf.* Winton[8]). Considering only lenticular grains of diameter greater than 10μ, if the numerical proportion with stellate hilums is less than 5 per cent. of the total number of starch grains, then wheat or barley or both may be present, and if the numerical proportion of grains of diameter greater than 40μ is less than 6·5 per cent. of the total number of grains, then wheat or barley starches, or both, are probably present with the rye. The observation that the numerical ratio of these grains of diagnostic value falls below the values usual for rye may be the first indication obtained that a small proportion of wheat or barley starch is present. Such an indication must be confirmed by a very thorough examination of the fibre, since a small proportion of wheat flour or barley meal will contribute only a very small proportion of fibre easily distinguishable from that of oats.

THE EXTENDED "LYCOPODIUM AND STARCH GRAIN" COUNTING METHOD.—The proportions by weight of endosperm or comminuted whole grain of rye and wheat (or barley) in a sample are determined as follows:—A mixture (of known composition by weight) of the sample and lycopodium is submitted to a counting process, by the technique described in Part II, in which the total number of lenticular grains of diameter greater than 10μ is determined. Lenticular grains with stellate hila, and lenticular grains with diameters greater than 40μ and 50μ are separately counted. With the appropriate factor derived from determinations with mixtures of known composition, the proportion by weight of rye flour (endosperm) or meal (comminuted whole grain) in the sample can be calculated either from the numerical proportion, with respect to lycopodium, of the grains with stellate hila, or, more accurately, from the similarly defined proportion of grains of diameter greater than 40μ.

Any surplus of "greater than 10μ, less than 40μ starch," beyond the requirement of the content of the rye grain product calculated from the data, is then used for calculating the proportion by weight of wheat (or barley) flour or comminuted whole grain, by means of the appropriate factors (see Tables II and III).

The following example of a sample of ground oats adulterated with the flours of rye and wheat illustrates the method. A mixture of 0·1000 g. of lycopodium and 0·8000 g. of the sample was made, and 9 fields per slide were counted (see Part II, p. 519, for technique).

TABLE I

No. of lycopodium spores (L) in 9 fields	No. of lenticular starch grains			No. of lenticular grains with stellate hila
	S>10μ	S>40μ	S>50μ	
225	537	11	2	14

Of the starch grains of diameter greater than 10μ (S>10μ), the low percentages of grains which are greater than 40μ in diameter (S>40μ), and also of those with stellate hila, show that lenticular starch other than that of rye is also present. A careful microscopical examination of the fibre showed that the other adulterant was wheat flour.

The calculations require the following basic data:

In mixtures of *equal* weights of lycopodium and rye flour it was found that each lycopodium spore corresponds to 0·73 to 0·92, average 0·80 [= factor $(R_t > 10\mu)/L$], rye starch grain of diameter greater than 10μ. The analogous factor for wheat flour, $(W_t > 10\mu)/L$, has values between 1·75 and 1·95 (average 1·87).

From the data in Table I, $(S > 10\mu)/L = 537/225 = 2{\cdot}387$ starch grains per lycopodium spore.

If all 537 starch grains are assumed to be rye, the weight percentage of rye flour in the sample is deduced by applying the factor $(R_t > 10\mu)/L$, thus:

$$\frac{\text{Wt. of rye flour}}{\text{Wt. of lycopodium}} = \frac{(S > 10\mu)/L}{(R_t > 10\mu)/L} = \frac{2{\cdot}387}{0{\cdot}80} = 2{\cdot}98$$

i.e. in the lycopodium and sample mixture there are 2·98 parts by weight of rye flour for each part of lycopodium.

But 8 parts of the sample were mixed with 1 part of lycopodium, therefore 8 parts of the sample contain 2·98 parts by weight of rye flour = 37 per cent. by weight of rye flour.

If, however, it is assumed that all the lenticular starch counted is derived from wheat flour, there are $\dfrac{(S > 10\mu)/L}{(W_t > 10\mu)/L} = \dfrac{2{\cdot}387}{1{\cdot}87} = 1{\cdot}28$ parts by weight of wheat flour in 8 parts of the sample, *i.e.* 16 per cent. by weight of wheat flour.

The large difference between the percentages by weight of total adulteration calculated from the $(S > 10\mu)/L$ data by assuming that the adulterant is either wholly rye flour or wholly wheat flour shows that the proportion of total adulteration cannot be stated until it is known which adulterant is present, or if both, their relative proportions (see p. 517). A method for calculating such proportions from data similar to those in Table I is shown in Tables II and III.

CALCULATION OF PROPORTIONS OF RYE AND WHEAT FLOURS IN THE SAMPLE.—(1) *By means of Starch Grains with Stellate Hila.*—The data are taken from Table I. The 537 starch grains, $S > 10\mu$, consist of R rye starch grains plus W wheat starch grains, and R in Table II is calculated from the number of starch grains, 14 (Table I), with stellate hilum and the proportion of such grains in pure rye flour.* From the respective starch grain to lycopodium (L) ratios, R/L and W/L, are calculated $\dfrac{R/L}{0{\cdot}8}$ and $\dfrac{W/L}{1{\cdot}87}$, the parts by weight of rye flour and wheat flour, respectively, in 8 parts of sample.

(2) *By means of Starch Grains greater than 40μ in Diameter.*—Since among approximately 300 grains of wheat starch of diameter greater than 10μ there is one of diameter greater than 40μ, allowance must be made for this when computing the proportions by weight of rye and wheat grain products from starch-size data if a preliminary calculation, where no allowance is made, shows that the relative number of wheat starch grains warrants the modification of the number of large grains used in calculating the content of rye product.*

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*An analogously determined correction is necessary in the case of wheat and barley starch mixtures if the governing diameter chosen is 35μ. The necessity for a correction does not arise with mixtures of rye starch and barley starch if the governing diameter chosen is 40μ, nor would it arise with mixtures of rye starch and wheat starch mixtures if the governing diameter chosen were 50μ, but the numerical proportion of rye starch grains of diameter greater than 50μ is too small to give the order of accuracy here attained unless a very large number of grains are counted.

TABLE II

	Rye flour				Residue as wheat flour				
	Total No. of rye starch grains $>10\mu$, (R)	R/L	$\frac{R/L}{0\cdot8}$	Wt. in sample Per Cent.	No. of wheat starch grains $>10\mu$, (W)	W/L	$\frac{W/L}{1\cdot87}$	Wt. in sample Per Cent.	Total wt. of adulteration Per Cent.
Min.	$\frac{14\times100}{11\cdot0^*}=127$	0·564	0·705	8·8	537−127=410	1·822	0·974	12·2	21
Av.	$\frac{14\times100}{7\cdot5^*}=187$	0·831	1·039	13·0	537−187=350	1·556	0·832	10·4	23
Max.	$\frac{14\times100}{5\cdot0^*}=280$	1·244	1·555	19·4	537−280=257	1·142	0·611	7·6	27

* Considering rye starch grains of diameter greater than 10μ, the minimum, average and maximum numerical proportions of grains with stellate hilum are 5, 7·5 and 11·0 per cent. respectively (see p. 514).

TABLE III

The symbols have the same significance as in Table II

	Rye flour				Residue as wheat flour				
	Total No. of rye starch grains $>10\mu$, (R)	R/L	$\frac{R/L}{0\cdot8}$	Wt. in sample Per Cent.	No. of wheat starch grains $>10\mu$, (W)	W/L	$\frac{W/L}{1\cdot87}$	Wt. in sample Per Cent.	Total Wt. of adulteration Per Cent.
Preliminary									
*Av.	$\frac{11\times100}{7\cdot5}=147$	0·653	0·816	10·2	537−147=390	1·73	0·927	11·6	22
Corrected for wheat starch $>40\mu$									
*Min.	$\frac{10\times100}{9}=111$	0·493	0·616	7·7	537−111=426	1·893	1·012	12·6	20
*Av.	$\frac{10\times100}{7\cdot5}=133$	0·591	0·739	9·2	537−133=404	1·796	0·960	12·0	21
*Max.	$\frac{10\times100}{6\cdot5}=154$	0·685	0·856	10·7	537−154=383	1·702	0·910	11·4	22

* Since the preliminary calculation and the results in Table II indicate 257–410 wheat starch grains, it is concluded that only 10 of the 11 grains of diameter greater than 40μ are due to rye. Of rye starch grains of diameter greater than 10μ, the minimum, average and maximum numerical proportions of those with diameter greater than 40μ is 6·5, 7·5 and 9 per cent., respectively (p. 514).

Bearing in mind the variations in the characteristics of natural products, the results in Tables II and III are consistent with one another, and show that the composition of the mixture is within a narrow range as compared with the extreme values which would be deduced by supposing that the whole of the starch was either that of wheat or rye. It is clear, however, that by choosing a factor for rye flour in the range 0·73 to 0·92 in place of 0·80 and a factor for wheat flour in the range 1·75 to 1·95 in place of 1·87, the range within which the composition falls is increased somewhat, and the calculated minimum proportion of total adulteration by weight would become approximately 19 per cent. in place of the values tabulated.

The results obtained, as described above, should be checked by repeating the counting process with another slide and then with a fresh lycopodium and sample suspension. In order to enhance the accuracy of the result, standard mixtures of approximately the composition deduced should be submitted to exactly the same mixing and counting processes as the sample, and the figures so obtained used to calculate the most probable composition of the sample.

The factors used in the calculations given above were derived from the examination of ranges of pure cereal products on the market about the time the analysis was made. It is to be expected that the characteristics of the cereals will depend upon the variety of the species, upon the locality where grown, and upon the climatic conditions existing during the growth and ripening of the grain. It follows that seasonal variations in the characteristics of grain are to be expected. It is, therefore, highly desirable that the analyst should obtain his own factors from an examination of genuine commercial grain or grain products on the market at the time of the analysis. It is not unlikely, therefore, that an extended examination of pure cereal products from all over the world will reveal a wider range of variation than has been found in the samples that I have examined, particularly in respect of the proportion of rye starch grains with stellate hila.

In view of the comparatively large variations found in the characteristics of the natural products, it has been considered unnecessary to introduce small corrections for the variations in the moisture-content of these air-dry materials. However, since the proportion by weight of moisture is about 11 per cent. (generally between 8 and 14 per cent.), it is desirable, for comparing results obtained at different times, to determine ratios on samples and mixtures at a definite moisture-content when mixed with lycopodium. When the moisture-content of a sample differs much from 11 per cent. the equivalent of the quantity used in the mixture can be readily calculated on an 11 per cent. moisture basis.

The directly determined chemical composition of the sample should be compared with that deduced from the microscopically determined composition, using accepted values of the chemical compositions of the ingredients. Any disaccord between the results, after allowance has been made for variations in the chemical composition of natural products, generally points to the presence of an ingredient which has been overlooked.

In discussing the extension of the "lycopodium and starch grain" count method to ternary and other mixtures, it may be noted that Wallis[4] determined the percentage composition of a binary mixture of wheat and barley flours by making use of the difference between the maximum sizes of wheat and barley starches. Bearing in mind the differences in principle and technique between the methods used by Wallis and that used here, it appears that the respective values recorded for the numerical proportions of wheat starch grains of diameter greater than 40μ in wheat starch and wheat flour (endosperm) are not inconsistent.

The method, illustrated above, is applicable to ground oats and other feeding-stuffs adulterated with rye flour and barley meal, or wheat flour and barley meal, and, in general, to the determination of the percentages by weight of each of two adulterants which have ingredients of suitable microscopical characteristics differing in as little as only one particular, that of maximum size of the particles.

II. A Microscope Projector Technique

To ensure as accurate as possible a count of a small proportion of large starch grains among many smaller grains, it is essential to have a considerable number of starch grains, say more than 50, not overcrowded, so that the grains will be flat, in each field counted, and an approximately equal number of lycopodium spores to act as a basis of reference. Nine fields are counted per slide, arranged as in Fig. 1, or if greater accuracy is required, 25 fields, arranged as described by Wallis.[5]

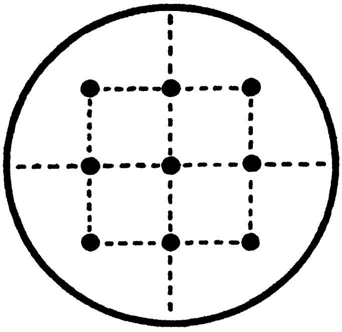

Fig. 1

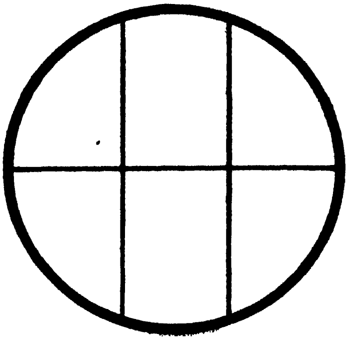

Fig. 2

It is a matter of some difficulty to divide into the appropriate ranges of size and to count all the starch grains, together with the admixed lycopodium spores, in a sufficiently densely covered microscope field when viewed through the eyepiece of a microscope. For this reason, a method has been devised whereby the image of the field is projected upon a vertical white screen. The microscope is tilted so that the axis of the optical system is horizontal, and a 30 candle-power Point-o-lite lamp and lens replace the mirror and lamp as source of illumination. The ordinary eyepiece is replaced by a projector lens, and the microscope is situated at such a distance from the screen that, with an 8-mm. objective, starch grains 50μ in diameter have an apparent diameter of 15 mm. This is checked by projecting on to the screen with this system a scale graduated in 0·01 mm. For convenience of counting, the field is divided into sections by means of fine wires stretched across an aperture placed between the projector and the screen (Fig. 2).

For distinguishing between grains falling within the different ranges of size, discs or loops of appropriate sizes are attached to the ends of rods in such a way that the discs can be brought easily into contact with the images on the screen. Thus, a solid disc of diameter 3 mm. is used to show whether starch grains are of diameter less than 10μ, whilst circular loops, 12 mm. and 15 mm. in diameter, of fine blackened wire, serve to show whether starch grains exceed 40 and 50μ in diameter, respectively. A transparent scale may also be used.

It is essential that adequate definition should be secured, for the following reasons:

(1) Complete aggregates of oat starch with circular outline may be mistaken for lenticular starch grains, with or without stellate hila, if the definition is poor. With good definition, the boundaries of the grains in the aggregates are clearly defined, and there is no confusion with lenticular grains having stellate hila.

(2) In commercial grinding and milling processes, lenticular grains very occasionally become flattened and their diameter considerably increased without rupture of the grain. Such objects may simulate large rye starch grains, and, if included in the total of large starch grains counted, lead to error. With good definition, such grains are easily recognised, as they have a very faint outline and an unsubstantial appearance, compared with the strong outline and robust appearance of the normal grains. These very occasional "ghosts" are neglected.

MOUNTING THE SAMPLE.—With the apparatus set up as described, the plane of the slide supporting the specimen is vertical, so that, unless the starch and lycopodium mixture is suspended in a highly viscous medium, the grains drift downwards, thus making accurate counting, etc., impossible. The difficulty is overcome in the following manner: The dry cereal and lycopodium mixture is mixed *thoroughly*, by rubbing gently with a flat-ended glass rod in a small beaker or mortar to break up aggregates of starch grains without smashing the grains. A sufficient quantity of water is then *thoroughly* incorporated, by gentle rubbing, to make a suspension of a soupy consistency. A small drop of this material is deposited on a slide, any small fragments of fibre are carefully removed by means of forceps, and a small drop of a commercial liquid glue is completely incorporated by means of a needle with the material on the slide. The quantity of material on the slide should be just sufficient to form a very thin permanent film covering the whole of the cover-slip when gently pressed to the slide. If the film is too thick, the suspended matter drifts across the field of view when the slide is supported in the projector. Under correct conditions the lenticular starch grains are oriented with their planes parallel to the plane of the glass slide.

There are at the present time several microscope projectors on the market, and one of these can be used with advantage in place of the microscope arrangement described above. In general, the stage of the projector is in a vertical plane when the projected image is received on a vertical screen, and hence the technique described above is applicable to these circumstances. If, however, the stage is in a horizontal plane, a less viscous mounting medium, such as described by Wallis (*loc. cit*), may be used.

SUMMARY

(1) A description is given of an extension of the lycopodium and particle count method to the quantitative microscopical analysis of certain ternary mixtures for which the simple method is inadequate.

(2) The microscopical determination of the proportion by weight of rye flour (or ground rye grain) in mixtures, including adulterated ground oats, containing starch-bearing products derived from wheat or barley grain, is described.

(3) Of rye starch grains of diameter greater than 10μ in diameter, there were found in rye flour

(*a*) Between 5 and 11 per cent. with stellate hila.

(*b*) Between 6·5 and 9 per cent. with a diameter greater than 40μ, whilst only a very small proportion of wheat starch grains of diameter greater than 10μ (about 1 in 300) exceeded 40μ in diameter.

(4) A microscope projector technique has been developed whereby the counting and classification of particles according to size, or other characteristic, are easily and accurately carried out.

I wish to thank Dr. J. J. Fox, the Government Chemist, for kind permission to publish this paper, and Mr. A. More for his helpful interest.

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DISCUSSION

Mr. WALLIS congratulated Dr. Griffiths on this work. He must have had a strenuous time in doing these very numerous counts, for in producing figures that could be used for the purposes of a standard test it was necessary to take special care. He was also glad to see a new worker in this particular field; he, personally, owed a debt of gratitude to Dr. Griffiths for entering it. He thought that Dr. Griffiths had been wise to study these different types of starch rather than to attempt to deal with the number of granules in starch, as had been attempted in Germany. He was also wise in choosing a minimum of 10μ in making the counts. He (Mr. Wallis) liked the projection method very much. He did not know whether, in doing the work, Dr. Griffiths had been able to arrive at any figure for the variation in the numbers occurring in any given material; such a figure would be quite interesting. He, personally, had found in materials such as linseed and senna that the natural variation in the material, due to different habitats and conditions under which they were grown, was somewhere about 15 per cent. It would be very interesting to know whether cereals showed similar variations.

Mr. L. EYNON thought that Dr. Griffiths had partly solved the difficult problem of distinguishing quantitatively between rye, wheat, barley and oats. He asked whether the results obtained by this method had been compared with those given by colorimetric methods, more particularly those for rye and wheat starches.

Dr. DYER said that the so-called "stellate hilum" of rye starch granules had sometimes puzzled him. He had noticed that often only quite a small minority of rye granules bore this characteristic appearance. He had doubt as to whether this appearance was properly described as a "stellate hilum" or whether it was merely the result of the bursting of the starch granules through over-ripeness.

Dr. D. W. KENT-JONES did not agree with the figure of 11 per cent. as the average moisture-content in materials of this sort; that was not his experience, and he thought that it ought to be 2 or 3 per cent. higher. Also, he did not approve of the suggestion of getting information from the percentage of gluten that could be washed out from such materials. The presence of other substances would alter the amount of gluten that could be washed out, so that a false conclusion might be indicated. He suggested that the test, however excellent, was a complicated one and, in view of the fact that high fees were not paid for such work, he would like to know how long such an analysis took.

Dr. GRIFFITHS, replying, remarked that in the range of factors that he had given there was an indication of the range of natural variation. There was, of course, an experimental error which came into these determinations, but his figures showed that in rye flour, of the starch grains greater than 10μ in diameter between 6·5 and 9 per cent. exceeded 40μ in diameter and 5 to 11 per cent. had stellate hila. The variation indicated by the first range was close to that referred to by Mr. Wallis, that of the second range was somewhat larger.

He, personally, had had no experience of the colorimetric methods mentioned by Mr. Eynon, but he understood from others who had, that they were not very reliable.

Dr. Dyer had raised a very interesting point. It seemed to be quite a possibility, if there were a central hilum in the grain, that during ripening the material had contracted, leaving these fissures. It was partly for this reason that he considered that the counting of starch grains with stellate hila afforded less reliable data than the counting of starch grains greater than 40μ in diameter. With regard to the method of analysis of rye middlings and wheat middlings, he did not know the method adopted by Dr. Dyer, but, naturally, the starch count method would give only the proportion of rye flour and wheat flour present, and then the proportion of each fibre present must be determined by some other process. He had done some work in connection with the determination of wheat fibre by a counting process, using the very characteristic "beaded" tissue of wheat. There was another alternative—if the proportion of wheat endosperm in the mixture were high ($>$ 50 per cent.) one could obtain a certain amount of gluten. Wheat flour was the only flour that gave gluten. The uncertainty of the factor to be used for converting gluten to wheat flour made the result an order of magnitude rather than a definite quantity.

In reply to Dr. Kent-Jones, Dr. Griffiths said that the moisture figure given was the average he had found for samples examined in the laboratory. It was quite easy to convert the factors to any other moisture-content which one might find. The gluten test was suggested only as being a very rough guide. It was agreed that the amount of gluten that could be washed out depended upon the other materials present. Some mixtures containing as much as 30 to 50 per cent. of wheat flour gave completely unsatisfactory results. Regarding the question of cost, he admitted that this was a tedious method. It was adopted to obtain a trustworthy figure when a figure had to be given and when no other method, shorter and quicker, was available.

The Determination of Boric Acid in Foodstuffs

By ROBERT S. ALCOCK, M.A., Ph.D.

The volumetric method of Thomson[1] for the determination of boric acid in foodstuffs has been shown to be liable to considerable errors when applied to samples of food containing large proportions of phosphates or of fat and small proportions (such as those found naturally in certain fruits) of boric acid. The errors were traced to co-precipitation of calcium borate during removal of phosphates, incomplete removal of phosphate, or volatilisation of boric acid with glycerol derived from fat during the ashing of the food in an alkaline condition. Monier-Williams[2] modified the process by removal, first, of calcium salts and, secondly, of phosphoric acid as magnesium phosphate, so as to avoid the first two causes of error. These causes of error were reduced to a minimum by another modification of the process,[3] based on work in this laboratory, in which the exact conditions of alkalinity required for precipitation of calcium phosphate and retention in solution of calcium borate were specified; the removal of fat before ashing the sample was a part of this modification, of which other later investigators have made slight changes.

As the conditions for removal of phosphate require great care and the results obtained by titration of the boric acid may be vitiated by accidental presence of phosphoric acid or carbonic acid, it is desirable to have a confirmation of the results by some test specific for boric acid. At one time all results obtained in this laboratory[4] were confirmed by a method involving ashing of the sample with excess of alkali, solution of the ash in a known excess of hydrochloric acid, addition of alcohol and turmeric solution in definite proportions, and comparison with known amounts of boric acid treated in the same way. This method was generally satisfactory, but failed when applied to meat products or to articles containing appreciable proportions of iron.

The present method was developed for the determination of boric acid in phosphate-rich ashes and makes use of the ready esterification of boric acid with methyl alcohol, distillation of the methyl borate and final titration of the boric acid as in the Thomson process.

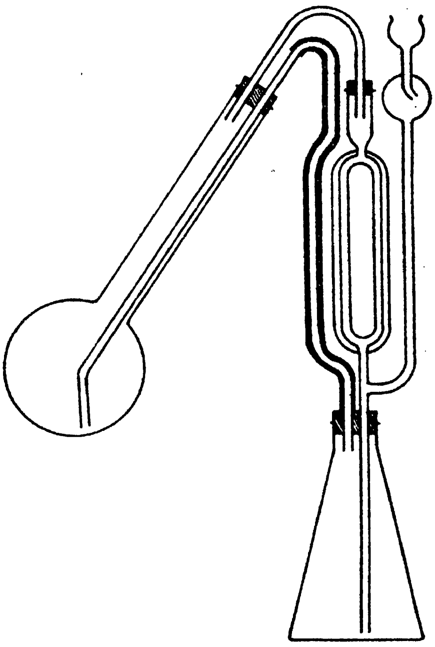

Fig. 1

APPARATUS.—The distillation is carried out in the apparatus here illustrated (Fig. 1). The acidified ash is boiled with methyl alcohol in a 300-ml. Kjeldahl flask, and the vapours are carried over into a double-surface condenser, the condenser being in a vertical position and the Kjeldahl flask inclined at 30° to it. The exit tube is elongated and dips below the surface of alkaline methyl alcohol in a 400-ml. conical flask. This flask stands on a tripod and gauze, and is strongly heated by a Bunsen burner. It is closed with a rubber stopper which carries, besides the condenser exit, another wide glass tube passing through a second hole in the bung of the Kjeldahl flask down into the methyl alcohol. The ascending limb of this tube must be lagged. This is conveniently done by enclosing it in a rubber tube.

Immediately above the stopper of the conical flask is a side-tube sealed on to the condenser outlet. This runs up close to the condenser and carries a splash-bulb and funnel. It serves to maintain atmospheric pressure inside the apparatus, to prevent possible losses through bumping in the receiver flask, and to make possible the washing out of the lower part of the condenser outlet.

PROCEDURE.—From 40 to 50 g. (or less when large amounts of boric acid are anticipated) of the sample are moistened with 10 ml. of 2 *N* sodium hydroxide solution. If much fat is present, it should be removed by solution in ether, as previously described.[3] The water is evaporated on a steam-bath, and the sample is ashed; there is no need to burn away all the carbon. The ash is transferred from the dish into the Kjeldahl flask, as little water as possible being used. The dish is finally washed with a few ml. of dilute sulphuric acid, and the ash in the flask is dissolved in a further quantity of the acid by warming. This removes most of the carbon dioxide and dissolves the lumps of ash. Methyl red is added, and 30 per cent. sodium hydroxide solution is run in until the colour changes to yellow. The liquid is concentrated to one or two ml. over a Bunsen flame, with continuous agitation. After cooling, 60 ml. of methyl alcohol and 1 ml. of methyl red solution are added.

Conc. sulphuric acid is then dropped in until, after shaking, the solution is strongly acid to the indicator. The flask is then attached to the apparatus, as is also the 400-ml. conical flask containing 0·5 ml. of *N* sodium hydroxide solution and a few drops of phenolphthalein solution. The Kjeldahl flask is heated and, when sufficient alcohol has collected in the conical flask, that too is strongly heated, so that the vapour bubbles vigorously through the acid liquid in the Kjeldahl flask. The flame beneath that flask is then adjusted so that 15 to 20 ml. of alcohol remain. If during the distillation the colour of the phenolphthalein in the conical flask is discharged, a further 0·5 ml. of sodium hydroxide solution is added.

After half-an-hour the flame beneath the Kjeldahl flask is replaced by a beaker of cold water, and as much of the methyl alcohol as possible is distilled up into it, and may be recovered later. The conical flask is removed, and the condenser tube, both inside and out, is washed into it with water. The remaining methyl alcohol is boiled off, and the solution is then made just acid to methyl red with *N*/10 sulphuric acid and boiled for a further five minutes to remove carbon dioxide. After cooling, the acidity is re-adjusted with *N*/20 sodium hydroxide solution until it is just not acid to methyl red. More phenolphthalein is added, and, after addition of 1 g. of mannitol, the titration is carried to the phenolphthalein change. A blank determination is made with water in place of a distillate. This result is usually of the order of 0·1 ml. of *N*/20 sodium hydroxide solution (1 ml. of sodium hydroxide solution ≡ 0·0031 g. boric acid).

Conditions of Distillation.—The conditions governing the distillation are illustrated in the following tables:

TABLE I

30 mg. of boric acid; 60 ml. of methyl alcohol; distilled 30 minutes

Acid	Methyl alcohol strength Per Cent.	Boric acid recovered Per Cent.
H_2SO_4	90	99·5
H_2SO_4	95	99·5
H_2SO_4	100	99·5
H_3PO_4	90	82·0
H_3PO_4	100	96·0

Table I shows that, given a sufficient strength of acid (excess of sulphuric over phosphate in the ash) amounts up to 10 per cent. of water in the alcohol do not influence the rate of distillation. When phosphoric acid is used the rate is affected.

TABLE II

1 g. of "artificial ash" plus boric acid; 60 ml. of methyl alcohol; excess of sulphuric acid; distillation 30 minutes

Boric acid mg.	Titration (less blank) $N/20$ NaOH ml.	Apparent boric acid mg.	Percentage error
0	0·05	0·15	—
5	1·65	5·12	2·4
10	3·28	10·15	1·5
30	9·77	30·18	0·6

Table II indicates the error likely to arise from phosphoric acid being carried over in the vapour. An artificial ash was made of equal weights of calcium chloride, kieselguhr, sodium sulphate and disodium phosphate. One g. of this mixture was placed in the distillation flask for each experiment. The phosphate coming over corresponds to some 0·15 mg. of boric acid (3 p.p.m. on 50 g. of sample). In practice, the figures for actual ashes seem to be less than this. Such a degree of accuracy is seldom required, but when very small amounts of boric acid are involved—of the order of 1 mg.—the distillation should be followed by the usual precipitation, after adding a drop or two of 10 per cent. calcium chloride solution. The phosphate comes over as a result of esterification, not through splashing, as more appears when a small amount of phosphate, acidified with sulphuric acid, is in the distillation flask, than when syrupy phosphoric acid itself (2 ml.) is used for acidification. Sulphuric acid is used, as the lower *p*H accelerates the distillation.

TABLE III

Boric acid; 60 ml. of methyl alcohol; sulphuric acid

Boric acid mg.	Time Minutes	Boric acid recovered mg.	Recovery Per Cent.
10	5	8·1	81
10	15	10·0	100
20	15	19·8	99
20	15	20·0	100
30	15	25·7	86
30	20	28·8	92
30	20	29·5	98
30	30	29·8	99·3
30	30	30·0	100

Table III summarises the experiments on the time required for distillation. In every instance the liquid in the receiver flask was boiled as vigorously as possible. It is seen that up to 20 mg. come over quantitatively in 15 minutes, while 30 mg. require longer. Half-an-hour's distillation is a usual routine time, as amounts of more than 30 mg. are seldom met with. If, however, on titration, more than 10 ml. of $N/20$ sodium hydroxide solution are required, the distillation can be carried on for a further half-hour period, when the remainder, if any, will be recovered.

TABLE IV

Sample	Weight g.	Boric acid added mg.	Titration (less blank) $N/20$ NaOH ml.	Boric acid found mg.	Recovery Per Cent.
Currants A	40	0	1·55	4·8	—
,, A	40	20	8·00	24·8	100
Flour B	50	0	0·3	0·9	—
,, B	50	20	6·7	20·8	99·5
,, B	50	40	13·3	41·2	100·7

Table IV gives two examples of the many determinations that have been made on various materials. It will be seen that the boric acid added to the sample before ashing was quantitatively accounted for in the final titration.

SUMMARY.—A method for the determination of boric acid in foodstuffs, using the distillation of methyl borate followed by a mannitol titration, is described.

A continuous steam-distillation apparatus, used in the method, is illustrated.

My thanks are due to Dr. J. J. Fox, the Government Chemist, for permission to publish this work.

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GOVERNMENT LABORATORY
CLEMENT'S INN PASSAGE
STRAND, LONDON, W.C.2

The Determination of Tartaric Acid as Lead Tartrate

BY C. H. MANLEY, M.A., F.I.C.

(*Read at the Meeting of the North of England Section, December* 14, 1935)

IN 1934, when undertaking the full analysis of a baking powder containing a mixture of rice, sodium bicarbonate, tartaric acid and acid potassium tartrate (concerning the percentages of which there had been some divergence of opinion), I sought for a new method for the determination of the total tartrate present, as an alternative to the usual one involving separation as acid potassium tartrate and subsequent titration with $N/10$ alkali.

The intention was, if possible, to weigh the tartaric acid in the form of one of its metallic salts. Of these, the lead salt, $PbC_4H_4O_6$, is one of the most sparingly soluble, its solubility at 20° C., according to Cantoni and Zachoder,[1] being nil. Like calcium tartrate, however, it is soluble both in acids and alkalis, but it was found possible to effect quantitative precipitation at room temperature from a solution previously rendered neutral to phenolphthalein.

In this method the use of the comparatively large amount of alcohol required in the precipitation and washing of acid potassium tartrate prior to its titration with standard sodium hydroxide[2] is dispensed with.

Lead acetate proved unsuitable as a precipitant, the results obtained with a neutralised solution of tartaric acid being in excess of those obtained by titration with standard alkali. Satisfactory results, however, were obtained with a sufficient excess of lead nitrate solution, after a two hours' precipitation period, in a solution neutralised to phenolphthalein.

At first no special attention was paid to the quantity of water used for washing the lead tartrate free from soluble salts, the object being to continue with a cold water wash until the filtrate showed no cloudiness with potassium chromate. It was subsequently found, however, that for the successful application of the method, a limited quantity of water must be used, as, notwithstanding the statement of Cantoni and Zachoder[1] to the contrary, lead tartrate was discovered to possess a slight solubility at 18°–20° C. amounting to 2 mg. per 100 ml. Washing with a cold saturated aqueous solution of dried lead tartrate effected no improvement.

The composition of the lead tartrate produced by the prescribed method was checked by conversion into lead sulphate (Pb in $PbC_4H_4O_6$: theory, 58·4 per cent.; found, 58·1 per cent.).

The following procedure was adopted, first, in testing the proposed method by employing it to assay samples of tartaric acid and acid potassium tartrate of known purity; and later, in applying it to the determination of the total tartaric acid in baking powders:

(*a*) TARTARIC ACID.—Two g. were dissolved in water, and the solution was made up to 200 ml. Several quantities of 20 ml. (= 0·2 g.) were made neutral to phenolphthalein by titration with 0·2 *N* sodium hydroxide solution in 100-ml. beakers, and in each case 15 ml. of 5 per cent. lead nitrate solution were added, and, after stirring, the white flocculent precipitates were left to stand for varying

TABLE I

TARTARIC ACID

Purity = 99·75 per cent. by titration of 0·5 g. with 0·2 *N* NaOH (mean of 99·6 and 99·9 per cent.).

Twenty ml. of a 1 per cent. solution (= 0·2 g.) used for each experiment.

Expt.	Precipitant	Time	Weight of lead tartrate g.	Tartaric acid, per cent. By titration	Tartaric acid, per cent. By lead tartrate method
42*b*	15 ml. of 5 per cent. $Pb(NO_3)_2$	½ hour	0·465	Average	98·3
43	,, ,,	1 ,,	0·466	100·3	98·3
40	,, ,,	2 hours	0·471		99·6
44	,, ,,	3 ,,	0·468		99·0
46	,, ,,	16 ,,	0·471		99·6
42*a*	,, ,, $Pb(C_2H_3O_2)_2$	3 ,,	0·480		101·5
39	,, ,, $Pb(NO_3)_2$	2 ,,	0·476		100·7*

* Precipitate washed with 50 ml. of saturated lead tartrate solution.

times. After this the precipitate was transferred to a Gooch crucible and washed with 50 ml. of water at 18°–20° C., the filtrate being tested with potassium chromate after 30 ml., 40 ml., and finally 50 ml. had passed through. By this time a constant opalescence was registered. By using the blue ring test for nitrates in a separate experiment with diphenyl-benzidine sulphate as reagent,[3] it was concluded that the excess of lead nitrate was removed after the passage of 35 ml. of water. The lead tartrate was dried to constant weight at 105° C. The factor for tartaric acid/lead tartrate is 0·423. The results obtained are given in Table I, together with the result obtained by substituting lead acetate for lead nitrate as precipitant. Ten ml. of 5 per cent. $Pb(NO_3)_2$ solution were found insufficient; 15 ml. were then used and found sufficient.

(*b*) ACID POTASSIUM TARTRATE.—Three g. were treated with hot water and phenolphthalein and neutralised by titration with 0·2 *N* sodium hydroxide solution. The solution thus obtained was cooled to room temperature and made up to 200 ml. Twenty ml. of this solution were then treated with 15 ml. of 5 per cent. lead nitrate solution, after which the procedure was identical with that followed in (*a*).

The results obtained are given in Table II, and, like those in Table I, they show that 2 hours are sufficient to ensure complete precipitation.

TABLE II

CREAM OF TARTAR

Purity = 100·0 per cent. by titration of 1 g. with 0·2 *N* NaOH (twice). Twenty ml. of a 1·5 per cent. solution (= 0·3 g.) used for each experiment.

Expt.	Precipitant	Time	Weight of lead tartrate g.	Acid potassium tartrate per cent. By titration of 0·3 g.	Acid potassium tartrate per cent. By lead tartrate method
49	15 ml. of 5 per cent. $Pb(NO_3)_2$	2 hours	0·566	99·3	100·0
47	,, ,,	16 ,,	0·563		99·5
50	,, ,,	2 ,,	0·564*		99·7*

* Precipitate washed with 50 ml. of saturated lead tartrate solution.

BAKING POWDER. — Following several preliminary experiments, the standardised lead tartrate method, with slight modification, was used for the determination of the total tartrate present in baking powders containing tartaric acid or acid potassium tartrate, or both, as the acid principle.

The presence of tartrate was first ascertained by treating about 1 g. of the baking powder with water, filtering, adding ammonia and a crystal of silver nitrate, and heating in the water-bath.[4] Other portions of the filtrate were tested for *phosphate, sulphate and chloride, any of which, if present, would interfere with the accuracy of the determination.*

If the sodium bicarbonate were exactly balanced in the baking powder by its equivalent of acid component, the lead tartrate could be precipitated directly from the aqueous solution freed from the rice or other starchy filler. As this is rarely so, however, the sodium bicarbonate being usually in slight excess, the following procedure was necessary:

One g. of baking powder was treated with a few ml. of cold water, and the starchy filler was filtered off on a weighed Gooch crucible, the filtrate being then made up to 50 ml. in a graduated flask. Twenty-five ml. of the filtrate were rendered just acid to methyl orange with 0·2 *N* nitric acid, the solution was boiled to remove carbonic acid and cooled, and 0·2 *N* sodium hydroxide solution was added to neutrality to phenolphthalein. Ten ml. of 5 per cent. lead nitrate solution were added, after which the normal procedure was followed.

For comparison, the tartrate was determined in the other 25 ml. of the tartrate solution by the method hitherto usually recommended, *viz.* precipitation as acid potassium tartrate and subsequent titration with 0·1 *N* sodium hydroxide solution.

The accuracy of this latter method was checked by employing it to assay the tartaric acid and acid potassium tartrate used in (*a*) and (*b*); these when titrated with 0·2 *N* sodium hydroxide solution had each shown approximately 100·0 per cent. With 0·2 g. of each compound the results were 99·0 per cent. for the tartaric acid and 98·7 per cent. for the acid potassium tartrate, indicating an error of approximately 1 per cent.

As the maximum figure for the total tartaric acid in a baking powder rarely exceeds 20 per cent., a 1 per cent. deficiency in this case would show 19·8 per cent. instead of the theoretical 20·0 per cent.—a comparatively small divergence. Actually, in two baking powders prepared in the laboratory the percentages of tartaric acid found both by the lead tartrate and the acid tartrate methods were slightly higher than theory. The results in Table III are given without the application of any correction, and indicate the close agreement between the old and the new methods.

TABLE III

TARTARIC ACID IN BAKING POWDER

0·5 g. used for each experiment

No. of baking powder	Exp.	Weight of lead tartrate g.	Tartaric acid, per cent. By lead tartrate method*	Tartaric acid, per cent. By acid pot. tartrate method	
(1)	60/61	0·242	20·5	20·7	Theory: 20·3
(2)	62/63	0·244	20·6	20·8	
(3)	56/57	0·216	18·3	18·3	
(4)	58/59	0·179	15·1	15·3	
(5)	64/65	0·245	20·7	20·7	
(6)	73/74	0·146	12·3	12·6	
(7)	75/76	0·127	10·7	11·1	
(8)	77/78	0·271	11·5	11·3	

* Percentage of tartaric acid $= W \times \frac{100}{0{\cdot}5} \times \frac{150}{355} = W \times 84{\cdot}6$, where W = weight of lead tartrate from 0·5 g.

If, instead of using 1 g. of baking powder, the extract from 2 g. is made up to 100 ml., 50 ml. of this may be used for the detection and determination of potassium, if present, the solution being acidified with dilute hydrochloric acid, and evaporated with platinum tetrachloride solution. From the potassium chloroplatinate obtained, the percentage of acid potassium tartrate may be calculated, and from this and the total tartrate the percentage of free tartaric acid is obtainable.

In the above Table, No. 5 was the only one containing acid potassium tartrate in addition to tartaric acid as the acid principle. In exceptional cases, when the weight of lead tartrate is less than 0·18 g., it is recommended that the determination should be repeated with a weight of baking powder sufficient to give such a concentration of tartaric acid in 25 ml. of extract that a minimum of 180 to 200 mg. of lead tartrate is obtained. This avoids a tendency towards low results, as in No. 6, in which, owing to the smaller quantity of precipitate, only 35 ml. of water were used for washing.

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CITY ANALYST'S LABORATORY
1, SWINEGATE, LEEDS, 1

An Improved Method for Determining Ethyl Alcohol in the Presence of Acetone

BY C. R. HOSKINS, B.Sc., PH.D.

THE necessity for an accurate method of determining ethyl alcohol in the presence of acetone has long been recognised. Two methods, involving the preliminary removal of the acetone, which have frequently been used in this laboratory, are those of Macoun[1] and of Hoff and Macoun.[2] The first depends on condensing the acetone with benzaldehyde in the presence of potassium hydroxide, the excess of benzaldehyde being subsequently removed. Whilst this method removes acetone quantitatively, an appreciable proportion of ethyl alcohol is lost; indeed, Macoun had observed losses amounting to as much as 4 per cent. of the alcohol present—losses for which no satisfactory explanation was offered. The second method removes acetone by condensing it with paraformaldehyde in the presence of alkali. Whilst material losses of ethyl alcohol have not been observed with this method, a disturbing factor has been the formation of traces of methyl alcohol.

If an aqueous alcohol solution containing acetone is distilled with excess of acid mercuric sulphate solution, the acetone is precipitated as a complex mercury compound (Denigès),[3] but the alcohol is not recovered quantitatively. The losses of alcohol in this operation have been studied, and the technique described below has been found to make these losses negligible.

Method.—The following solutions are necessary:—(1) Acid mercuric sulphate containing 50 g. of mercuric oxide, and 125 ml. of conc. sulphuric acid per litre. (2) Potassium oxalate, approximately 300 g. per litre. (3) Sodium formate, approximately 100 g. per litre.

The amount of acetone in the alcohol solution must be ascertained approximately. A rapid method is that of Adams and Nicholls,[4] which measures colorimetrically the indigo formed on condensing the acetone with *o*-nitrobenzaldehyde in the presence of alkali.

This having been done, an amount of alcohol solution containing not more than 1 ml. of acetone is introduced into a flask of approximately 750 ml. capacity. For each 0·1 ml. of acetone to be removed are added 25 ml. of the acid mercuric sulphate solution and 0·2 ml. of the sodium formate solution. The flask is connected with an efficient condenser for refluxing, and its contents are heated (see below), with frequent agitation, at such a rate that clouding takes place in approximately ten minutes. The flame under the flask is then lowered so as to keep the solution at about the same temperature for ten to twelve minutes. A few ml. of distilled water are poured down the condenser to wash any acetone which may have condensed there into the flask. At the end of the ten to twelve minutes, excess of potassium oxalate solution—12 ml. for each 100 ml. of mercuric sulphate—is poured through the condenser to precipitate the excess of mercuric sulphate as mercuric oxalate. The flask is cooled, and the condenser is again rinsed with distilled water, after which the flask is removed and connected with an ordinary distilling apparatus. Since the final volume of liquid may be as much as 400 or 500 ml., it is advisable to collect at least 150 ml. of distillate and to redistil this, preferably from an alkaline solution, to a smaller volume.

The formation of the mercury complex takes place at approximately 80° C. By avoiding any appreciable rise above the clouding temperature of the solution, and by precipitating the excess of mercuric sulphate when condensation with the acetone is complete, the oxidising action of the mercuric sulphate on the alcohol is greatly reduced. The addition of sodium formate, which appears to be preferentially oxidised by the mercuric sulphate, also slightly lessens the oxidation of the alcohol during the initial heating period.

The following table of results shows how small is the loss of ethyl alcohol. In each experiment acetone was added to 100 ml. of ethyl alcohol solution of known strength, and the mixture was treated as described. All normal precautions against loss of alcohol were taken, distillates being collected by means of an adaptor dipping below the surface of the liquid in the receiver. The distillate from the mercuric oxalate precipitate occasionally gave a slight aldehyde reaction with Schiff's reagent; and although the effect of this on the specific gravity of the distillate was negligible, the opportunity was taken, when redistilling to the original volume of 100 ml., of removing the aldehyde by distilling from alkaline silver nitrate. Specific gravities were determined at 60°/60° F., the volume of ethyl alcohol being obtained from the official Spirit Tables. Each distillate was tested for the presence of acetone, and in the rare cases in which it was found, the amount was determined colorimetrically. In the table the amounts of alcohol recovered have been corrected, where necessary, for the acetone present, it being assumed as a near approximation that a 1 per cent. by vol. acetone solution has the same specific gravity as a 0·7 per cent. by vol. ethyl alcohol solution.

	Original solution		Final solution			Loss of alcohol	
Acetone ml.	Specific gravity at 60°/60° F.	Alcohol ml.	Specific gravity at 60°/60° F.	Acetone ml.	Alcohol ml.	ml.	Per Cent.
0·2	0·99317	4·75	0·99318	0·02	4·73	0·02	0·4
0·2	0·98681	9·81	0·98692	nil	9·72	0·09	0·9
0·2	0·98160	14·51	0·98172	nil	14·39	0·12	0·8
0·6	0·99311	4·80	0·99318	nil	4·74	0·06	1·2
0·6	0·98737	9·33	0·98750	nil	9·22	0·11	1·2
0·6	0·98160	14·51	0·98169	nil	14·42	0·09	0·6
1·0	0·99317	4·75	0·99318	nil	4·74	0·01	0·2
1·0	0·98681	9·81	0·98696	nil	9·68	0·13	1·3
1·0	0·98160	14·51	0·98172	0·04	14·59	0·14	1·0

A few experiments were carried out to determine the loss of methyl alcohol under the same conditions. The results of three of them are given in the following table. The percentages of methyl alcohol were obtained from the tables of Klason and Norlin.[5]

	Original solution		Final solution			Loss of alcohol	
Acetone ml.	Specific gravity at 60°/60° F.	Alcohol ml.	Specific gravity at 60°/60° F.	Acetone ml.	Alcohol ml.	ml.	Per Cent.
1·0	0·99358	4·50	0·99389	nil	4·28	0·22	4·9
1·0	0·98626	10·03	0·98655	nil	9·80	0·23	2·3
1·0	0·98050	14·70	0·98090	nil	14·36	0·34	2·3

It will be observed that the losses with methyl alcohol are greater than with ethyl alcohol, but there is evidence that part, if not all, of this increased loss occurs during distillation.

For purposes of comparison, acetone was removed from an ethyl alcohol solution by the method now described and by the two other methods mentioned. The methyl alcohol formed in the paraformaldehyde method was estimated colorimetrically by means of Schiff's reagent after oxidation of the methyl alcohol to formaldehyde. In each instance 1 ml. of acetone was removed from an ethyl alcohol solution of sp.gr. 0·98683 at 60°/60° F., containing 9·79 ml. ethyl alcohol in 100 ml.

	Final solution				Loss of ethyl alcohol	
Method	Special gravity at 60°/60° F.	Acetone ml.	Methyl alcohol ml	Ethyl alcohol ml.	ml.	Per Cent.
Mercuric sulphate	0·98699	0·04	nil	9·63	0·16	1·6
Paraformaldehyde	0·98697	nil	0·06	9·62	0·17	1·7
Benzaldehyde ..	0·98727	0·08	nil	9·36	0·43	4·4

In view of the loss of alcohol and the considerable time necessary for its operation, the benzaldehyde method must be considered inferior to the other two. There appears to be little to choose between the mercuric sulphate and the paraformaldehyde methods where methyl alcohol formation is not a disadvantage; but its presence, even in traces, is undesirable—indeed, inadmissible if it be necessary to decide whether the alcohol present has been methylated or not.

The new method has been used for several months in a section of this Laboratory with consistently trustworthy results.

I am indebted to Mr. G. F. Sheppard for much valuable criticism, and to Dr. J. J. Fox, the Government Chemist, for permission to publish this method.

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The Determination of Bismuth as Phosphate

BY W. R. SCHOELLER, PH.D., F.I.C., AND D. A. LAMBIE, B.SC., A.I.C.

(*Read at the Meeting, May* 5, 1937)

A METHOD for the determination of bismuth in high-grade ores, in which the metal is weighed as phosphate, has been described by Schoeller and Waterhouse.[1] The process has been extensively used by us, and has lately been the subject of further investigation, the results of which are given in this paper.

What caused us to study the method afresh was the observation that, whilst very serviceable on the whole, it was found occasionally to give fluctuating results, more particularly with substantial amounts of bismuth; in such cases, the deviations from the observed mean were either positive or negative, reaching but usually not exceeding 0·5 per cent. These irregularities were eventually proved to be due to contamination of the phosphate with sulphate, derived from the bismuth sulphide by oxidation with nitric acid.

PRECIPITATION OF BISMUTH PHOSPHATE IN PRESENCE OF SULPHATE.—The co-precipitation of sulphate is illustrated in Exps. 1 to 4, in which a uniform quantity of sulphuric acid was added to solutions of bismuth nitrate prior to precipitation of the phosphate. The washed phosphate precipitate was decomposed with sodium carbonate solution, and the acidified filtrate precipitated with barium chloride.

Exp.	Bismuth taken	Sulphuric acid added	Sulphuric acid found in $BiPO_4$
	g.	g.	g.
1	0·0523	0·1000	0·0020
2	0·1020	0·1000	0·0039
3	0·3044	0·1000	0·0112
4	0·5025	0·1000	0·0180

In these experiments the sulphate-content of the unignited precipitate is very nearly a linear function of the quantity of bismuth.

When bismuth phosphate is precipitated from an acid solution containing sulphate, we must assume that it carries down a sulphate comparatively low in bismuth, for the bismuth result at first shows a positive error; on continued ignition, the sulphate is converted into oxide, and the error becomes negative. Such is the case in Exps. 5 to 8, in which a known amount of bismuth was dissolved in nitric acid, the solution precipitated with hydrogen sulphide, and the sulphide converted into phosphate according to Schoeller and Waterhouse's directions:

Exp.	Bismuth taken g.	Bismuth found 1st weighing g.	Bismuth found Last weighing g.	Error 1st Wt. g.	Error Last Wt. g.
5	0·0556	0·0561	0·0554	+0·0005	−0·0002
6	0·1023	0·1030	0·1021	+0·0007	−0·0002
7	0·3032	0·3065	0·3021	+0·0033	−0·0011
8	0·5395	0·5441	0·5375	+0·0046	−0·0020

These tests show that, for quantities of bismuth of the order of 0·1 g., the error incurred in Schoeller and Waterhouse's procedure is negligible. With large amounts of bismuth, however, the absolute error becomes appreciable.

As the assay of bismuth ores unavoidably involves sulphide precipitation as a step in the separation procedure, and subsequent solution of the sulphide in nitric acid (with partial oxidation of the sulphur to sulphuric acid), we argued that precipitation of the bismuth from the resultant solution by means of sodium carbonate, and solution of the washed precipitate in nitric acid, would yield a nitrate solution free from sulphate, from which pure bismuth phosphate would be precipitated. This improved method, which we are applying to the determination of bismuth in high-grade ores, is as follows:

AUTHORS' METHOD.—A quantity of powdered ore equivalent to less than 0·3 g. of metallic bismuth is digested with strong hydrochloric acid, with the object of decomposing any wolframite and galena present. The acid is evaporated to a small bulk, strong nitric acid is added, and the contents of the beaker are evaporated almost to dryness on a steam-bath. The nitrates are converted into chlorides by two evaporations with strong hydrochloric acid. The dry residue is digested with 5 ml. of strong hydrochloric acid, which is then diluted with 20 ml. of hot water, the insoluble matter being filtered off and washed with warm *N* hydrochloric acid. The filtrate is boiled with 1 to 2 g. of very fine pure iron wire; when the solution has become colourless, the boiling is continued for another 20 to 30 minutes, hot water being added towards the end so as to reduce the acidity to less than 0·5 *N*. The metallic precipitate is filtered off by decantation on a filter containing a small spiral of iron wire, washed with boiling water, returned to the beaker, and dissolved in hot hydrochloric acid and bromine.

The filtrate from the iron precipitation should always be tested for complete precipitation as follows:—It is saturated with hydrogen sulphide, any precipitate being collected and reserved (see below, A). The main solution is freed from bromine by evaporation, diluted, and treated with hydrogen sulphide. The precipitate is collected, washed free from iron with acidulated hydrogen sulphide water, returned to the beaker, and digested for an hour on a hot plate with yellow sodium sulphide solution. The insoluble fraction is collected on the filter previously used, and washed with hot 3 per cent. sodium sulphide solution.

The alkaline filtrate is boiled with 10 to 15 g. of ammonium sulphate and left to settle.[8] Any precipitate is collected and heated, together with precipitate A above, with nitric and sulphuric acids until the former is expelled and copious fumes of the latter are given off. The residual acid, while still warm, is diluted with 1 : 1 and then with *N* sulphuric acid; any lead sulphate is filtered off, and the filtrate is tested for bismuth by the colorimetric iodide method.

After having been extracted with sodium sulphide, the sulphide precipitate is returned to the beaker, the paper is cleaned with hot nitric acid (1 : 1), and the precipitate is digested hot with strong nitric acid until the residual sulphur has fused into transparent globules. The nitrate solution is filtered through a small pad of filter-pulp, which is washed with 5 per cent. nitric acid. The filtrate is neutralised with sodium carbonate, of which an excess of 1 g. is added, as well as 0·5 g. of potassium cyanide, and the solution is boiled for a short time. The precipitate is allowed to settle completely, collected on a tight pad of filter-pulp, and washed with 2 per cent. sodium carbonate solution containing cyanide. It is advisable to treat the filtrate with hydrogen sulphide water, and to test any precipitate for bismuth, as with A above. The carbonate precipitate and pad are returned to the beaker, and heated with not much more than enough nitric acid to effect solution. The solution is once more filtered through a small pad of filter-pulp into a 600-ml. beaker, the pulp suspended in the liquor being gathered and squeezed with a glass rod; washing is effected with 5 per cent. nitric acid.

The filtrate (less than 100 ml.) is now ready for phosphate precipitation. It is left to cool, treated with 1 : 1 ammonia till turbid, cleared with 2 ml. of strong nitric acid, heated to boiling, and precipitated with 30 ml. of 10 per cent. diammonium phosphate solution (for 0·25 to 0·3 g. Bi), added, drop by drop, from a burette during continuous agitation. The first portion of precipitant is added very slowly; this results in a coarsely crystalline precipitate. When precipitation is complete, the liquid is diluted with 300 ml. of boiling distilled water and left to settle for an hour on a hot plate. The precipitate is collected on a tared porous porcelain crucible and washed with hot 2 per cent. ammonium nitrate solution containing a few drops of nitric acid per litre. Alternatively, the precipitate is collected on a 9-cm. No. 40 Whatman filter, and washed as before. The paper may be dried and ashed separately, but we have actually found this precaution unnecessary; in serial analyses we transfer the wet filter to a tared porcelain crucible, dry the contents on a hot plate, and gently heat them on an asbestos mat until the paper has charred. The carbon is burnt away at low temperature. The ignition is completed on a triangle over the full flame of a Bunsen burner. The weighed precipitate should again be ignited and weighed.

If the filtrate from the phosphate precipitate is tested with hydrogen sulphide it should remain colourless, but occasionally a negligible pale-brown coloration is produced.

Notes on the Process.—(i) We prefer to operate on quantities of bismuth not exceeding 0·25 or 0·3 g., because the accuracy is not increased by the use of large amounts. On the contrary, the precipitation conditions realised by our procedure tend to give closer results when the quantity of metal is kept below 0·3 g.

(ii) When the sulphide precipitate is digested with yellow sodium sulphide for the purpose of extracting arsenic and antimony, a small, variable amount of bismuth is usually found in the filtered extract. This is recovered by boiling with ammonium sulphate, the sodium sulphide being converted into the ammonium salt, in which bismuth sulphide is insoluble.

(iii) Alkali cyanide is added in the precipitation of sulphate-free bismuth carbonate by sodium carbonate, in order to extract any copper and silver which may be present.

(iv) After several years' practical experience, we are satisfied that the phosphate method is the most accurate and convenient process for the determination of bismuth in high-grade ores. Hillebrand and Lundell, who give preference to the gravimetric determination as bismuth oxide,[3] assert that the phosphate method should not be considered in accurate analyses, no reason being given by them for its rejection. On the other hand, Schoeller and Waterhouse's procedure for the precipitation of the phosphate is reproduced in the compilation of select methods for use in reference analyses, published by the Committee of German Metallurgical Chemists.[4]

Our reasons for giving preference to the phosphate method are, that the phosphate is the most tractable bismuth precipitate known, being "a white, heavy, crystalline precipitate resembling lead sulphate, quite insoluble in water or in very dilute nitric acid, depositing and filtering quickly, unchanged by ignition, and not easily reduced."[1] The ignition is carried out, as described above, in ordinary or in porous porcelain crucibles. The use of ordinary crucibles and paper filters is an invaluable advantage in serial work.

The determination of bismuth as oxide, on the other hand, involves its precipitation by means of ammonium carbonate. The basic carbonate precipitate is by no means an ideal one as regards settling, filtering, and washing. It is also liable to contamination with basic sulphate; this can be corrected by re-precipitation, but such work has to be conducted with great care, as bismuth carbonate is slightly soluble in ammonium carbonate, a fact admitted by Hillebrand and Lundell. The filtrates from the carbonate precipitation should therefore be tested for bismuth. The greatest drawback of the oxide method is the ignition of the precipitate. Bismuth oxide cannot be ignited in contact with filter fibre, and must therefore be separated from the dried filter, the part adhering to the paper being dissolved in nitric acid and the solution evaporated to dryness. The oxide is fusible, and in the molten state rapidly destroys the glaze of porcelain crucibles. Hence, Hillebrand and Lundell advise ignition in platinum, a rather unattractive procedure, on account of the risk of accidents to the crucibles and the number of costly vessels required in serial work.

SUMMARY.—Bismuth phosphate, precipitated from solutions containing sulphate, is liable to be contaminated with sulphate, which loses sulphur trioxide on ignition. A modified phosphate method for the assay of high-grade bismuth ores is described, in which the interference of sulphate is overcome by an intervening

precipitation with sodium carbonate. The advantages of the phosphate method over the gravimetric determination as bismuth oxide are discussed.

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THE SIR JOHN CASS INSTITUTE
ALDGATE, LONDON, E.C.3

DISCUSSION

Dr. B. S. EVANS said that the authors had mentioned the presence of sulphur trioxide in the phosphate precipitate; it was not quite clear whether this replaced P_2O_5 or whether it was simply adsorbed in some way. It was amazing how much sulphuric acid could be precipitated in this manner; considering that there was only 0·1 g. of sulphuric acid present, it meant that 0·5 g. of bismuth precipitated contained about 20 per cent. of it.

Dr. Schoeller had also referred to the elimination of sulphuric acid by the precipitation of bismuth carbonate, and later on he spoke of the objection to the determination as oxide because it had first to be precipitated as basic carbonate, which was liable to contamination with basic sulphate. If that were so, one would think that the method wanted much care in avoiding that contamination of basic sulphate in basic carbonate.

Dr. Schoeller, with characteristic modesty, had not mentioned a paper recently published in *Industrial and Engineering Chemistry* in which the authors put forward a method that seemed to be substantially that of Schoeller and Waterhouse. (They had not claimed an original method.) The figures given confirmed Schoeller and Waterhouse's original paper to a very gratifying extent.

Dr. SCHOELLER, replying, said that regarding the mode of combination of the sulphur trioxide in the precipitate, he was unable to give any definite information. All he could say was that at the beginning of the ignition there was a positive error, and at the end a negative one. This led to the inference that an acid sulphate was precipitated with the phosphate, and that the conversion of the sulphate into oxide by stronger ignition caused the negative error. The use of the modified method described in the present paper would do away with the slight inaccuracy.

As to the contamination of the carbonate precipitate with sulphate it should be borne in mind that Hillebrand and Lundell used ammonium carbonate as a precipitant, whilst the authors used the sodium salt. The former, being weaker in its action, might yield a precipitate not altogether free from sulphate, which would contaminate the oxide to be weighed; hence double precipitation might be necessary. The authors, on the other hand, used a stronger alkali, and the bismuth carbonate thus obtained was converted into phosphate—an operation in which traces of sulphate, if any still remained, would not interfere.

The amount of bismuth that went into the sodium sulphide filtrate and was recovered by ammonium sulphate was very small; it might amount to 2 mg. It seemed to vary according to the presence or absence of such elements as arsenic, antimony and copper. The determination of the recovered bismuth by the colorimetric process was convenient and accurate, and much to be preferred to a gravimetric method.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF SMALL QUANTITIES OF STRYCHNINE IN THE PRESENCE OF CAFFEINE (COMPOUND SYRUP OF GLYCEROPHOSPHATES)

SIMMONDS's method (ANALYST, 1914, 39, 81) for the determination of small quantities of strychnine in the presence of a large excess of quinine, which depends on the solubility of quinine ferrocyanide and the insolubility of strychnine ferrocyanide in strongly acid solution, can be readily adapted for mixtures of caffeine and strychnine, such as are obtained by extraction from Compound Syrup of Glycerophosphates B.P.C.

The mixed caffeine and strychnine can be extracted from the syrup by adding a large quantity (5 g.) of citric acid to 50 ml. of syrup and, after making the solution alkaline with ammonia, extracting five times with chloroform. After drying, the residue of anhydrous caffeine and strychnine is weighed.

To meet the present problem, the procedure of the original method can be simplified, since it is found that caffeine does not appear to be co-precipitated with the strychnine; hence re-precipitation is unnecessary.

The following results of some experiments made to ascertain this point show the simplicity of the method:

Solution A:	2·500 g. of anhydrous caffeine in 250 ml. of water.
Solution B:	20 ml. of Liquor Strychninae Hydrochlor. B.P. (containing 0·8622 per cent. w/v of strychnine) sufficiently evaporated to eliminate alcohol, and made up to 50 ml.; 3 ml. of dilution = 0·0103 g. of strychnine.
Solution C:	Freshly-prepared 5 per cent. potassium ferrocyanide solution.
Solution D:	25 per cent. v/v sulphuric acid.

		Strychnine
1.	25 ml. A + 5 ml. C, overnight	No precipitate
2.	25 ” A + 5 ” C + 1 ml. D, overnight	” ”
3.	25 ” A + 5 ” C + 10 ” D, ”	” ”
4.	25 ” A + 3 ” B + 1 ” C, ”	Trace
5.	3 ” B + 25 ” water + 1 ml. C + 1 ml. D, overnight	0·0100 g.
6.	25 ” A + 3 ” B + 1 ml. C + 1 ml. D, ”	0·0101 g.
7.	25 ” A + 3 ” B + 1 ” C + 10 ” D, ”	0·0102 g.
8.	25 ” A + 3 ” B + 1 ” C + 1 ” D, 4 hours	0·0098 g.
9.	25 ” A + 3 ” B + 1 ” C + 1 ” D, 4 hours, re-precipitated overnight	0·0095 g.

The most suitable procedure for the determination would appear to be: Dissolve the weighed caffeine and strychnine from 50 ml. of syrup in 25 ml. of water to which is added 1 ml. of 25 per cent. v/v sulphuric acid, warming if found necessary. Cool, add 1 ml. of freshly-prepared 5 per cent. potassium ferrocyanide solution, stir to induce precipitation and leave for some hours, preferably overnight. Filter through a 7-cm. No. 1 filter-paper and wash well with water slightly acidified with sulphuric acid. Place the funnel in the neck of a separator, pierce the tip of the filter-paper, and wash in its contents successively with 10 ml. each of 10 per cent. ammonia, water and chloroform, added from the precipitation beaker. Extract three times with chloroform, evaporate with 5 ml. of alcohol, dry the residue, and weigh.

For re-precipitation, only slight washing of the precipitate is necessary. After chloroform extraction, re-extract with 30 ml. of water containing 1 ml. of 25 per cent. v/v sulphuric acid, in three portions. Boil the acid extracts to eliminate chloroform, and re-precipitate with 1 ml. of 5 per cent. potassium ferrocyanide.

D. C. Garratt

L.C.C. Chemical Laboratories
County Hall, London, S.E.

OPTICAL ACTIVITY OF PREPARATIONS OF SQUILL

In a recent communication from this laboratory (Analyst, 1937, p. 192) it was pointed out that both Tinct. Scillae B.P. 1932 and Acetum Scillae B.P. 1932 showed a marked laevorotatory optical activity.

The quantitative aspect of this matter has now been investigated and it has been shown that Tinct. Scillae B.P. 1932 has an average optical rotation of —2·0°, whilst that of Acetum Scillae B.P. 1932 is —3·5°. The optical activity of the Acetum thus approaches twice that of the Tincture, although the same amount of Squill is used in the manufacture of both these preparations. As it is generally recognised, from the therapeutic point of view, that the Tincture is the more active preparation, it would thus appear that the higher optical activity is associated with the lower therapeutic value.

It was considered possible that the development of optical activity might be due to hydrolysis of the squill glycosides giving rise to a laevorotatory sugar. The following experiment was therefore carried out in order to see whether this hydrolysis could be carried further:—A sample of Tinct. Scillae B.P. 1932, known to be of full physiological activity and having an optical rotation of —1·8°, was treated with 1 per cent. of hydrochloric acid at laboratory temperature, and measurements of the optical rotation were made from time to time. It was found that the optical rotation slowly increased, reaching a maximum of —4·3° in two weeks. A simple pharmacological test carried out on the treated sample gave indications of decrease in physiological activity; although an isolated experiment, this was probably significant.

A sample of Acetum Scillae B.P. 1932 similarly treated showed a rise in optical rotation from an initial value of —3·5° to a maximum of —4·65°.

Leo McGraghan

Analytical Laboratory
Messrs. Brady & Martin, Ltd.
Newcastle upon Tyne, 2

DYESTUFFS FOR DEVELOPING LATENT FINGER-PRINTS

Further experiments have been made on the applicability of Waxoline dyestuffs for the development of latent finger-prints, by dusting the dyestuff powder over the article under examination, and then fixing the impression of the finger-print by exposure to acetic acid fumes and to steam (*cf.* Analyst, 1937, 192). The following (I.C.I.) Waxoline colours are particularly suitable for this purpose and cover a variety of shades:—Waxoline Yellow OS, Waxoline Orange AS, Waxoline Red AS, Waxoline Violet 2BS. An appropriate dyestuff can therefore be selected according to the colour of the object under examination, so that the impression of the finger-print will show up in contrast; for instance, the pale yellow dyestuff would be suitable for dusting over such articles as japanned tin boxes.

H. A. Thomas

Imperial Chemical Industries, Ltd.
(Dyestuffs Group)
Hexagon House
Blackley, Manchester

THE DETECTION OF INHALED HYDROCYANIC ACID

THE use of hydrocyanic acid for fumigation purposes has become very prevalent, not only for ships but also for warehouses and private houses. Reports on the subject have been issued from time to time (*cf.* Reports on Public Health and Medical subjects to the Ministry of Health, Nos. 19, 60 and 72, and ANALYST, 1931, **56**, 46).

We were asked to examine the viscera from a case of suspected poisoning by hydrocyanic acid, and we were successful in showing the presence of this substance in the blood of the deceased. It has been suggested to us that there are very few cases on record where hydrocyanic acid has been found in the blood of those who have died by inhaling an atmosphere containing a very small amount of this gas, and that our results may be of interest to others.

An elderly couple, each over 70 years of age, were found dead in a house next door but one to a house in which fumigation with hydrogen cyanide had been carried out. The fumigation had commenced at about 9.20 a.m., but the bodies were not found until about 10.30 p.m., although there was evidence to show that both persons were alive and apparently well at noon.

The intermediate house was used as a buffer house with windows and doors open all day long. Furthermore, although all the houses were "attached," the one in which the fatalities took place was built five years after the others in the row, and there was no obvious sign of intercommunication; neither did a smoke test yield any positive result.

When the viscera were received, comparatively small quantities were examined for hydrocyanic acid, but with negative or inconclusive results. We then operated by steam distilling 250 ml. of the blood from the lungs, until 15 ml. of distillate had been collected. On two separate 5-ml. quantities we carried out the Prussian blue and sulphocyanide reactions as described below. In each case we obtained slight but definite reactions. The amount of cyanide found was certified as approximating to one milligram of hydrocyanic acid per litre of blood. The stomach contents were free from all but the smallest trace of hydrocyanic acid.

Blank distillations, carried out before the addition of the blood, and after the first 15 ml. of distillate from the blood had been collected, gave negative results.

The verdict at the inquest was accidental death due to cyanide poisoning.

PRUSSIAN BLUE TEST.—About 5 ml. of the distillate are made alkaline with two or three drops of 5 per cent. sodium hydroxide solution. To this are added two drops of 5 per cent. ferrous sulphate solution and one drop of 3 per cent. ferric chloride solution. The mixture is then allowed to stand for two minutes, gently heated, and acidified with dilute hydrochloric acid. Sufficient hydrochloric acid only is used to clear the liquid; there should not be a great excess of acid. Traces of cyanide may show only after fifteen to thirty minutes, but on standing overnight a blue precipitate settles out.

SULPHOCYANIDE TEST.—About 5 ml. of the distillate are heated with one drop of yellow ammonium sulphide solution for fifteen minutes on the water-bath. Dilute nitric acid is then added until the yellow colour of the solution is (just) entirely destroyed. Ferric alum solution is then added, drop by drop, until the maximum colour is obtained.

G. D. ELSDON
J. R. STUBBS

LANCASHIRE COUNTY LABORATORY
COUNTY OFFICES, PRESTON

The determination of traces of cyanide in cases in which death has resulted from the inhalation of hydrocyanic acid presents difficulties, for the amount of the poison present may be extremely minute and, owing to its volatile nature, it tends to disappear. As the writers of the above note have shown, the only chance of detecting cyanide lies in the examination of blood or lung tissue, and material should therefore be sent to the analyst in a well-stoppered bottle as soon as possible.

Under the most favourable conditions it sometimes happens that even the Prussian blue and sulphocyanide tests fail. In those circumstances the following procedure, which has proved successful in my hands, may be tried. The steam distillate, which should be collected in a conical flask, is treated with a few drops of basic lead acetate solution to fix the sulphur compounds which are always present in the distillates from viscera, and especially in those from lung tissue. A few drops of dilute sulphuric acid are then added until the liquid is faintly acid. A drop of silver nitrate solution of about $N/10$ concentration is placed on a microscope slide, and this is inverted over the top of the conical flask and left in position in a warm place for at least 30 minutes, after which it is removed and covered with a cover-glass; microscopic examination may then reveal the presence of the characteristic crystals of silver cyanide. Alternatively, or in addition, the alloxan test may be tried (*cf. Ann. chim. anal.*, 1921, **3**, 179; Abst., ANALYST, 1921, **46**, 334). With both these tests I have obtained positive results on more than one occasion with distillates which had failed to give either the Prussian blue or the sulphocyanide reaction. I would add, however, that I am not satisfied that either of these tests establishes absolute proof of the presence of cyanide, although, taken in conjunction with all the facts of the case concerned, they will leave little doubt in the minds of most people.

In connection with the investigation of this class of cases I would observe that the post-mortem findings should in any given instance reduce the question down to the alternatives of carbon monoxide and hydrocyanic acid poisoning. A blood examination will establish the presence or absence of carbon monoxide. Finally, in the absence of carbon monoxide, positive reactions with either or both of the tests mentioned above should establish beyond all reasonable doubt the cause of death.

G. ROCHE LYNCH

ST. MARY'S HOSPITAL
LONDON, W.1

Report of the Essential Oil Sub-Committee to the Analytical Methods Committee

REPORT No. 13

THE DETERMINATION OF ESTERS

THE Essential Oil Sub-Committee makes the following recommendations for the determination of esters in essential oils. Numerous experiments carried out by members of the Sub-Committee have shown that, unless the conditions of the tests are standardised somewhat closely, considerable variations in results between different operators and in different laboratories are likely to occur.

The following reagents are required:

Alcohol (90 per cent. by volume).

Alcoholic potassium hydroxide: approximately $N/10$ prepared by diluting alcoholic potassium hydroxide, approximately $N/2$, with 90 per cent. (by volume) alcohol and standardising by titration with $N/10$ acid using phenolphthalein as indicator.

Alcoholic potassium hydroxide: approximately $N/2$ prepared by dissolving 33 g. of potassium hydroxide of reagent purity in 1 litre of 95 per cent. (by volume) alcohol, allowing to stand, and decanting or filtering the clear liquid.
Sulphuric acid or hydrochloric acid: $N/2$.
Phenolphthalein: 0·2 per cent. solution in 60 per cent. alcohol.

METHOD OF DETERMINATION.—Two g. of the oil, or other suitable quantity so that the amount of alkali added is at least double that required for saponification, are weighed into the saponification flask; 5 ml. of freshly well-boiled and neutralised alcohol are added, and the free acid is titrated with $N/10$ alcoholic potassium hydroxide solution, using 0·2 ml. of phenolphthalein solution as indicator (*Note* 1). The result of the titration is calculated to acid value (mg. of KOH required for the neutralisation of 1 g. of the oil). To the neutralised solution in the flask are then added 20 ml. of $N/2$ alcoholic potassium hydroxide solution, and the whole is boiled under a reflux condenser for 1 hour (*Note* 2), at the end of which time the excess of alkali is titrated immediately with $N/2$ acid, using an additional 0·5 ml. of phenolphthalein solution as indicator. At the same time a blank determination is carried out by boiling for 1 hour under a reflux condenser 5 ml. of alcohol, 20 ml. of $N/2$ alcoholic potassium hydroxide, and 0·2 ml. of phenolphthalein solution, and then titrating immediately with $N/2$ acid after the addition of a further 0·5 ml. of phenolphthalein solution. In the case of bergamot oil, there may be a re-appearance of the pink colour on standing; this should be ignored (*Note* 3).

The difference between the two titrations is calculated to the percentage of esters in the usual manner, using the appropriate factor. Those for the most commonly occurring esters are as follows:

Bornyl acetate	0·0981	Santalyl acetate	0·1311
Geranyl acetate	0·0981	Methyl salicylate	0·0760
Linalyl acetate	0·0981	Geranyl tiglate	0·1181
Menthyl acetate	0·0991	Linalyl benzoate	0·1290

The following should be noted:

Note 1. With oil of wintergreen and oil of sweet birch, the free acid should be determined in a separate experiment by shaking 5 g. of the oil with 25 ml. of water, and titrating with $N/10$ aqueous sodium (potassium) hydroxide solution, using 1 ml. of *phenol red* (0·04 per cent. in 20 per cent. alcohol) as indicator. The saponification should be carried out without the preliminary neutralisation of the free acid, and from the volume of alkali required the equivalent of that used in the separate determination of the free acid should be deducted.

Note 2. With oil of wintergreen and oil of sweet birch, the boiling should be continued for an hour and a half.

Note 3. It is proposed to deal with the examination of bergamot oil in a later report.

RESULTS.—The members of the Sub-Committee have from time to time carried out determinations in their own laboratories on samples of various ester-containing oils circulated for this purpose. In the accompanying table are shown the results obtained on eight samples of such oils. From a consideration of these results amongst others we are of opinion that the maximum variation in the percentage of esters estimated by this method should not exceed ±0·7 per cent.

RESULTS OF ESTER DETERMINATION IN OILS

Member	Lavender Linalyl acetate Per Cent.	Bergamot Linalyl acetate Per Cent.	Bergamot Linalyl acetate Per Cent.	Bourbon geranium Geranyl tiglate Per Cent.	Pine Bornyl acetate Per Cent.	Pepper-mint Menthyl acetate Per Cent.	Spike lavender Bornyl acetate Per Cent.	Methyl salicylate Per Cent.
1	42·6	40·4	37·5	24·5	37·3	8·0	2·7	100·0
	42·6	40·4	37·3	24·6	37·3	8·0	2·5	99·9
			37·8	24·9	37·3	7·9	2·3	
2	42·1	40·2	37·7	25·2	37·5	7·3	2·4	—
	42·2	40·3						
	42·3	40·3						
	42·4	40·4						
		40·3						
		40·2						
		40·4						
3	41·6	—	38·3	25·2	37·6	7·7	2·3	99·6
			38·0	25·2	37·4	7·8	2·1	
4	42·2	40·7	38·0	24·4	37·2	7·2	2·1	99·1
	42·4	40·9	37·7	24·4	37·2	7·3	2·0	99·2
5	42·1	40·4	37·7	25·6	37·2	7·8	2·3	99·7
	42·4	40·5	38·1	25·1	36·6	7·5	2·2	99·5
6	42·6	40·4	—	—	—	—	—	—
	42·3	40·5						
7	42·7	41·4	—	—	—	—	2·7	99·2
	42·8	41·5					2·6	
8	41·9	40·5	38·0	25·2	38·1	7·7	—	99·2
9	—	40·9	37·6	25·0	37·7	7·7	2·6	99·6
		40·5	37·8	25·5	37·5	7·4	2·3	99·0
		41·3	38·1	25·1	37·5		2·2	
		40·6			37·8			
Range ..	41·6–42·8	40·2–41·5	37·3–38·3	24·4–25·6	36·6–38·1	7·2–8·0	2·0–2·7	99·0–100·0
Mean ..	42·3	40·6	37·8	25·0	37·4	7·64	2·35	99·6
Standard deviation	0·32	0·31	0·26	0·37	0·30	0·26	0·23	0·31

(*Signed*)

W. H. Simmons (*Chairman*), C. T. Bennett, S. W. Bradley, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, John H. Seager, Gilbert E. Smith, J. Sutherland, T. Tusting Cocking (*Hon. Secretary*).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF LEEDS

Annual Report of the City Analyst for 1936

The total number of samples examined was 2218, of which 138 were taken informally. Nine of the informal, and 161 of the formal samples were adulterated.

Potted Beef.—Two of 7 samples were adulterated, one containing 48 per cent. and the other 49 per cent. of starchy filler; in each case the amount of starch was 4·6 per cent. It is contended that such products should be sold as "Potted beef pastes." The wholesale vendor of the first sample (which was taken in course of delivery to the retailer) was prosecuted and found guilty, but the case was dismissed under the Probation of Offenders Act on payment of 14s. 6d. costs.

No proceedings were instituted in connection with the second sample, as the wholesaler had intimated at the time of the sale that the preparation was meat paste.

Dust in Leeds, Halifax and Huddersfield.—A second series of exposures, in which soft paraffin wax was used instead of prepared lard, was made during the six months October, 1935, to April, 1936, and the results obtained are given in Table I.

Table I

Station	Total dust		Arsenic oxide		Lead		Copper	
	mg. per sq.ft.	cwts. per sq.mile	mg. per sq.ft.	cwts. per sq.mile	mg. per sq.ft.	cwts. per sq.mile	mg. per sq.ft.	cwts. per sq.mile
Leeds								
*No. 1. Centre (Market Buildings)	1700·0	933·0	0·582	0·320	5·190	2·850	0·970	0·533
No. 2. Residential (Spring Bank)	526·0	289·0	0·216	0·119	0·563	0·309	0·216	0·119
No. 3. Industrial (Goodman Street)	112·0	61·5	0·043	0·024	0·193	0·106	nil	nil
No. 4. Residential (Knostrop)	1160·0	637·0	0·304	0·167	0·990	0·544	1·270	0·697
No. 5. Centre (Market)	6050·0	3320·0	2·880	1·580	18·300	10·050	2·520	1·384
Halifax								
No. 1. Centre (Over Clock Chamber)	5930·0	3255·0	1·422	0·780	14·690	8·000	1·900	1·044
No. 2. Industrial (Public Library)	2070·0	1136·0	0·634	0·348	25·500	14·000	5·620	3·085
No. 3. Residential (Northowram Hall)	942·0	516·0	0·427	0·234	11·200	6·150	0·642	0·353
Huddersfield								
†No. 1. Industrial (Disused Mill Room)	160·0	87·8	0·013	0·007	0·086	0·047	nil	nil
No. 2. Centre (Market Hall Clock Tower)	3180·0	1745·0	1·810	0·994	4·350	2·390	14·800	8·130
No. 3. Residential (Ravensknowle)	1770·0	972·0	0·532	0·292	2·180	1·198	1·330	0·730

* Tampered with—apparently not seriously. † Removed and placed vertically in a window.

Owing to the widely different conditions under which the plates have been exposed, any general comparison between the quantities found in different areas would give a false impression. Thus, as an illustration from the Leeds deposits, we know from the rain-gauge deposits that Hunslet usually gives figures about treble those at Headingley, yet the dust collected on the plate at Goodman Street, Hunslet, is only about one-fifth of the amount collected at Spring Bank, Headingley. Similarly, of the two plates exposed at Market Buildings, Leeds, one has collected three and a half times as much dust as the other, owing to differences in the manner of exposure.

Fortunately, three plates (one plate in each town) were exposed under similar conditions, namely, in the open air, but protected from rain, and these may be compared one with another, although the areas in which they were exposed were of different types. The Leeds area was in the centre of the town, and the Halifax and Huddersfield areas were residential. The figures for these three plates are given below:

	Cwts. per square mile			
	Total dust	Arsenic oxide	Lead	Copper
Leeds—Market Roof ..	3320·0	1·580	10·050	1·384
Halifax—Northowram ..	516·0	0·234	6·150	0·353
Huddersfield—Ravensknowle	972·0	0·292	1·198	0·730

As one would expect, the Leeds plate collected the largest amount of dust and of arsenic, lead and copper; the Huddersfield plate collected nearly twice as much dust as that at Halifax, but contained only about the same amount of arsenic, one-fifth the amount of lead and twice as much copper.

Proportions of Arsenic, Lead and Copper.—The figures in Table II are of similar order to those obtained from the six Leeds dusts examined in 1932 (*cf.* ANALYST, 1933, **58**, 471).

TABLE II

	Arsenic oxide		Lead		Copper	
	Per Cent.	p.p.m.	Per Cent.	p.p.m.	Per Cent.	p.p.m.
LEEDS						
*No. 1. ..	0·034	342	0·306	3055	0·057	570
No. 2. ..	0·041	410	0·107	1070	0·041	410
No. 3. ..	0·038	384	0·172	1725	nil	nil
No. 4. ..	0·026	262	0·085	854	0·109	1095
No. 5. ..	0·047	476	0·302	3025	0·041	416
HALIFAX						
No. 1. ..	0·024	240	0·248	2480	0·032	321
No. 2. ..	0·031	307	1·234	12340	0·272	2720
No. 3. ..	0·045	453	1·188	11880	0·068	682
HUDDERSFIELD						
†No. 1. ..	0·008	80	0·053	534	nil	nil
No. 2. ..	0·057	570	0·137	1370	0·465	4650
No. 3. ..	0·030	300	0·123	1230	0·075	752

* Tampered with—apparently not seriously. † Removed and placed vertically in a window.

This table is more useful than Table I for purposes of comparison because the proportions of the metals given are independent of the amount of dust collected, and therefore all the plates can be compared one with another.

Arsenic is found in greatest proportion in the centres of Leeds and Huddersfield, and in the residential area of Halifax, Huddersfield having the greatest percentage, and Leeds and Halifax being about equal.

Lead is found in greatest proportion in No. 2 (Industrial) and No. 3 (Residential) at Halifax, the percentages being far greater than on any other plate and so high that they call for some explanation. In Leeds and Huddersfield the centre of the town contains the highest percentage of lead, Leeds containing more than Huddersfield. Copper is also found in an unusually high percentage in the central area, Huddersfield. Halifax has the next largest percentage, in an industrial area, and Leeds has the third largest percentage in No. 4 area, which is near a copper works.

C. H. MANLEY

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1937

THE total number of samples analysed was 1,465, of which 1,422 were bought informally.

"HOME-MADE" "FULL FRUIT STANDARD" JAM.—A sample of blackcurrant jam was labelled "Full Fruit Standard," and in another place as "Home-made." It is unlikely that a small shopkeeper producing a home-made article would be a signatory to the agreement with the Food Manufacturers Federation. Nevertheless, there is nothing illegal in the use of the Federation label by a person making home-made jam, and as no proof was forthcoming of the origin of the sample, no action was taken.

COMPOUND BISMUTH LOZENGES.—In response to a demand for this article, for which the B.P. description specifies lozenges containing 0·15 g. of bismuth carbonate, 0·15 g. of magnesium carbonate and 0·3 g. of calcium carbonate, tablets were supplied of a heart shape which were seriously deficient in all three ingredients. The vendor stated that he kept stocks both of these tablets and of the official lozenges and apologised for having supplied the former in error. These were asked for by customers as "heartshape bismuth tablets," and were supplied by a wholesale firm for sale as "indigestion tablets." He promised to take steps to ensure that no confusion should arise in the future.

SODA MINT TABLETS.—This article is contained in the B.P. Codex under the name of Compound Sodium Bicarbonate Tablets, and one of the synonyms is "Soda Mint Tablets." Each tablet should contain, according to the Codex formula, 0·324 g. of sodium bicarbonate and 0·008 g. of ammonium bicarbonate, together with small amounts of saccharin and oil of peppermint. One sample contained the correct weight of sodium carbonate but no ammonium bicarbonate. A second sample, bought from the same shop a month later, was found to be of the correct B.P.C. quality. No action was taken.

ARTIFICIAL VINEGAR.—Seven informal samples, sold as vinegar, consisted of artificial vinegar. In each case the sampling officer visited the shop and explained the difference between the two articles and the conditions under which they should be sold. Artificial vinegar is often sold wholesale as "pure vinegar," and some retail vendors may not be aware that what they are buying under this name is really the synthetic product.

A sample of malt vinegar, bought informally, consisted of artificial vinegar, and an official sample bought two days later, had the same composition. The stock barrel was labelled "Guaranteed absolutely pure vinegar." On a blackboard in the shop, however, was written in chalk, "Pure Malt Vinegar, 2d. pint." The vendor was prosecuted and fined 20s.

H. H. BAGNALL

METROPOLITAN BOROUGH OF CHELSEA

ANNUAL REPORT OF THE PUBLIC ANALYST FOR 1936

OF the 400 samples analysed, 301 were taken formally and 4 of these were adulterated. Eight of the 99 informal samples were adulterated.

CITRUS FRUIT POWDERS.—A sample of Orangeade Powder and one of Lemon Barley Powder were each reported as adulterated, as they contained tartaric acid instead of citric acid, the acid natural to citrus fruits.

MEDICATED SWEETS.—A sample of iodine and blackcurrant pastilles contained 0·046 per cent. of iodine. A sample of linseed, liquorice and chlorodyne tablets contained neither morphine nor prussic acid, which would have rendered the seller liable under the Dangerous Drugs Act and the Pharmacy and Poisons Act, but the sale of these sweets indiscriminately to children is dangerous. Sometimes, liking the strong flavour, they eat too many; on the other hand, there is the risk, which is perhaps greater—that some people take so-called medicated sweets or wines with impunity, and think that they can do the same with the properly medicated preparation obtained from a druggist. T. McLachlan

Department of Scientific and Industrial Research

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

Report and Observations in the Year ended March 31st, 1936*

The 22nd Report on Atmospheric Pollution embodies, as in previous years (*cf.* Analyst, 1936, 61, 257), the Report of the Standing Conference to the Co-operating Bodies; the Report of the Atmospheric Pollution Research Committee; the Report of the Superintendent of Observations, which includes tables and graphs; an Appendix on Observations on Ultra-violet and Visible Rays in Rochdale, and the General Deposit Tables. Photographs are also included of the Experimental Apparatus for measuring Sulphur in Air in relation to Wind Directions, the Standard Lead Peroxide Gauge for estimation of sulphur in the atmosphere, and the combined apparatus for measuring sulphur dioxide (by the volumetric method) and suspended impurity.

The number of the deposit gauge stations has been increased during the year from 98 to 115, and the number of automatic filters from 14 to 15, whilst the number of lead peroxide cylinders exposed has decreased from 45 to 42. The special intensive survey of pollution for which preparation has been in progress for some time has been arranged to take place in Leicester. Renewed interest has been taken in obtaining records of sulphur dioxide concentration, and the apparatus now designed (photograph) records the frequency of the winds from each of 8 sectors, and at the same time exposes a corresponding sector of the lead peroxide fabric, which can subsequently be analysed by sectors. An apparatus constructed to measure the conductivity of rain water is shortly to be tested. With a view to finding the best way to estimate the amount of dust in a stain obtained by drawing air through filter-paper, the possibility of calibrating optical densities of stains by direct weighing is being explored.

In considering the general trend of atmospheric pollution over a period of years, as shown by the tables and graphs, there is definite ground for belief that the smoke abatement movement has had real effect. It has to be remembered that increases in pollution in certain cases may be due to increased industrial activity. Taken generally, the total deposit curves show a large decrease in pollution before the industrial depression set in. Suspended matter, on the other hand, although showing an improvement in the air in certain cases, in others indicated a marked increase in impurity. Sunshine observations show that winter sunshine in London, compared with that at Kew, has risen from 20 to 52 since 1881.

Lime in Deposit.—A table is included in the Report showing the deposit of lime in metric tons per sq. km. with the same figure expressed as per cent. of total solids. A large addition to the number of stations estimating lime occurred in September, so that comparison for the months April to August is not possible in most cases. For the summer months the lime (as per cent. of total solids) averaged 7·1, and for winter (October–March) 5·57.

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* Published May 19th, 1937, pp. 128. Obtainable at Adastral House, Kingsway, W.C.2. Price 6s. net.

MEASUREMENT OF pH.—In all stations at Burnley the water was consistently acid except for one month; Coventry showed consistently alkaline water. Two Liverpool stations had acid water, but two other Liverpool stations showed alkaline water on a few occasions. Salford's water was acid (with pH under 5·5 throughout the year), as also that of Wakefield, whilst at Southport it was slightly alkaline in 2 months, and Rochdale's acid water only once had a pH exceeding 5·5. There was a greater tendency towards acid water during the winter. The highest alkalinity was found during June and July last year, and this year during May and July.

Acidity (as sulphuric acid) and *Alkalinity* (as ammonia), estimated by titration, do not necessarily agree exactly with the pH values, and the table indicates constant acidity in nearly all stations. The only stations showing constant alkalinity were Hove, with a five month's record, and Kingston-upon-Hull all the year, whilst Birmingham (West Heath) was alkaline for every month except February. From the table the tendency appears to be toward increased acid pollution.

AUTOMATIC FILTER.—In general, higher impurity is shown in winter than in summer, December–February being the worst and May–September being the best periods. The highest concentration of impurity at any of the stations was recorded for Stoke-on-Trent, where the summer minimum was about twice the winter maximum at Cardiff. In order to bring out the trend of the automatic filter records over a period of years, where a sufficiently long series of records is available, the average hourly concentration of sooty matter for the whole summer and winter have been calculated and graphs drawn. For some stations definite improvement is indicated; for example, London generally shows improvement except for Victoria Street, but in some places there is increase in pollution, *e.g.*, Cardiff and particularly Coventry.

SULPHUR POLLUTION.—*Volumetric Method.*—Sulphur in the air is at once seen from the tables to be a winter product. London showed the highest average pollution, but the highest concentration figure for the year was for Salford (Regent Road) in December, but as this was more than three times any other figure for Salford it was doubtless due to some specific cause. It must be remembered that measurement of sulphur concentration is made at a particular place and does not denote conditions at any great distance from that place. Returns obtained by the lead peroxide method were made from 41 stations, 10 also using the volumetric method. The exceedingly high sulphur pollution in London calls for investigation and remedy.

ULTRA-VIOLET RADIATION BY THE ACETONE AND METHYLENE BLUE METHOD.—The Research Committee are still engaged on the examination of methods for the measurement of ultra-violet radiation with the object of providing a standard one. There are certain objections to the acetone and methylene blue method. Useful information may, however, be obtained by using the figures obtained by it for comparative purposes; thus the Cardiff figure (Cardiff is a city remarkably free from pollution) is about double the next highest figure—for Kingston-upon-Hull. Further useful comparisons can be made from figures for the centre and outskirts of cities. The obstruction of the radiation by smoke could only be effectively examined by comparing radiation received in a city with that which it should receive if no city were there, and the nearest to that is a comparison with surrounding country on the windward side.

MEASUREMENT OF ATMOSPHERIC POLLUTION IN AMERICA.—An investigation extending over 2 years was carried out in 14 of the largest cities of the United States, Owens's automatic filter and jet dust counter, and the Smith Greenburg impinger for weight and composition of suspended matter, being used. The Aitken nuclei counter was also used, and measurement of daylight taken with the Macbeth illuminometer, and of ultra-violet light with the Reutschler meter. No measurements of deposit were taken and the method adopted was to apply the methods mentioned throughout a week in each city. The results are recorded in Public Health Bulletin No. 224. The average shade number of all the automatic filter records between 8 a.m. and 4 p.m. in the cities tested was, for winter, 1·3, and the corresponding figure in London, Glasgow and other British cities was 2·4; from these results the conclusion was drawn that British cities were nearly twice as heavily polluted as American.

RECORD OF OBSERVATIONS.—The maximum and minimum monthly deposits as metric tons per sq.km. were:—*Tar*: Bradford 37, Dewsbury (Whitley) and Huddersfield 2; *carbonaceous matter other than tar*: Burnley (Parker Lane) 414, Glasgow (Mearnskirk Hospital) 31; *insoluble ash*: Liverpool (Netherfield Road) 1125 (next highest, St. Helens 575), Glasgow (Mearnskirk Hospital) 44; *ash of insoluble matter*: London (Finsbury Park) 570, Wakefield (Clarence Park) 106; *total solids*: Liverpool (Netherfield Road) 2277, (next highest Burnley [Parker Lane] 1545), Glasgow (Mearnskirk Hospital) 309; *rainfall*: Rochdale 101 mm., London (Victoria Park) 49.

The figures for the current year indicate an increase for tar, and both carbonaceous matter other than tar and insoluble ash indicate rather worse atmospheric conditions. The same applies to soluble ash and total solids. For the latter the greatest increase was at London (Finsbury Park), with Dewsbury (Ravensthorpe) next. Stations showing an increase in all components of deposit compared with the "General Average" were Bournville Village and Works, Dewsbury, Halifax, Sheffield (Nether Green), and Southport (Bedford Road Park).

D. G. H.

Annual Report on Alkali, &c., Works for 1936

THE Seventy-third Report of the Chief Inspectors to the Ministry of Health and to the Department of Health for Scotland deals with methods adopted for preventing the emission of offensive gases in a very wide range of industrial processes. Not only are the processes registrable under the Act reviewed, but many instances are cited in which complaint has arisen in connection with processes outside the scope of the Act. The question of smoke emission also receives more attention than it has done in previous Reports.

The Public Health (Smoke Abatement) Act, 1926,* provides, in effect, that a prosecution for the emission of smoke, other than black smoke, shall not succeed when adequate and proper plant for preventing the creation and emission of smoke is provided and efficiently maintained, and also used in a proper and skilful manner. Efficient stoking goes to the root of the second part of this provision.

The subject of smokes and fumes from burning colliery spoilbanks and from coal carbonisation processes is dealt with in this connection, and the Report suggests that greater efforts at abatement could, and ought to, be made.

Smoke arising from pottery kilns, brick works, blast furnaces, rivet works, and boiler plants is also dealt with.

WASTE GASES FROM ELECTRIC POWER STATIONS.—In connection with electric power stations, the following figures supplied by the London Power Co. are interesting as showing the magnitude of the task of purifying the waste gases from a large power station:

Total weight of coal fired: 430,887 tons (about 50 tons per hour).
Average sulphur-content of coal: 0·91 per cent.
Total volume of gas treated: 200 thousand million cb.ft. (dry at N.T.P.).
Average sulphur emission (898 works tests): 0·025 grain (as S) per cb.ft. of dry gas at N.T.P.
Equivalent of sulphur eliminated by gas washing: 3611 tons.

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* Reproduced, as from October 1st, 1937, in Sections 101–106 of the Public Health Act, 1936.

Arsenic Works.—The condensation of arsenious oxide has been satisfactory, the average content of gases escaping from the calcination of arsenical ores being 0·038 grain of As_2O_3 per cb.ft., accompanied by a total acidity of 0·65 grain.

The amount of white arsenic and arsenic soot produced in Cornwall is still small, the figure in 1935 being 172 tons as compared with 3207 tons in 1924. In Sweden the output is of the order of 150 tons per day. The price is low and the lodes now worked in Cornwall are poor in arsenic, so that calciners are finding difficulties in disposing of soot with an As_2O_3 content of between 20 and 30 per cent. A partial refinement appears to be the only means of making a material acceptable to the refiners and avoiding the cost of storage or the danger of exposed heaps of arsenical soot.

Cement Production Works.—Cement has been in high demand throughout the year, and the increased production has resulted in a number of complaints about dust emission. Encouraging progress, however, has been made with the problem of preventing the emission of dust, and electrical precipitation is now practised at a number of works and is in course of installation in many others. The dust concentration can readily be reduced by this process to a concentration below 0·5 grain per cb.ft.

The Report also gives the customary statistics relating to salt cake, sulphuric acid, tar and ammonia.

Connecticut Agricultural Experimental Station

FORTIETH REPORT ON FOODS AND TWENTY-EIGHTH REPORT ON DRUGS

The Department of Analytical Chemistry of the Station, under the direction of Dr. E. M. Bailey, is primarily concerned with analytical work relating to inspection and control of commercial fertilisers, feeding stuffs, foods, drugs and insecticides, but it also does work for other departments of the State, and collaborates with the Association of Official Agricultural Chemists in its studies of analytical methods.

The present Report summarises the work done in 1935, mainly in connection with food and drug control. Among the subjects of interest discussed are the following:

Orangeade.—The regulation in Connecticut and other States requires orangeade to contain at least 15 per cent. of orange juice. Considerable quantities of orange base concentrate are now sent to local distributing agencies, such as fountains and dairies, where it is diluted and made into beverages of the orangeade type. Being an orange product, its nutritional virtues due to vitamin *C* are usually stressed in advertising. According to Bessey and King (*J. Biol. Chem.*, **1933**, **103**, **693**) the vitamin-content of undiluted orange juice is of the order of about 0·6 mg. per ml. By mere dilution, and assuming that there is no destruction of vitamin *C* in the preparation of the concentrate, orangeade beverage should contain about 0·09 mg. of the vitamin. Some loss or destruction of vitamin is to be expected in the process of converting juice into a commercial concentrate, and there may be a further reduction through over-dilution.

Fresh juice expressed from oranges in the laboratory without special precautions gave results for vitamin *C* agreeing well with those of Bessey and King.

The ash from the concentrates was substantially the same as from fresh juice. Several samples officially submitted gave the following results:

	Ash g. per 100 ml.	Vitamin *C* (ascorbic acid) mg. per ml.	Approximate juice content (basis of ash) Per Cent.
Concentrate I	0·373	0·289	—
Beverage made from I ..	0·048	0·015	12
Orangeade	0·064	0·019	16
Concentrate II	0·409	0·390	—
Beverage made from II ..	0·074	0·045	18
Orange juice, canned ..	—	0·450	—
Orange juice fresh ..	0·41	0·510	—
Do. ..	0·41	0·510	—

A fair interpretation of these figures is that the beverages made from the concentrates contain from 12 to 18 per cent. of orange juice, but that the vitamin *C* content has suffered some impairment. A sample of orangeade submitted by a local health department contained only 0·012 mg. of vitamin *C* per ml.

DETECTION OF TEASEED OIL IN OLIVE OIL.—The following test, devised by Fitelson, differentiates teaseed oil from any of the other food oils in present use. A few drops of the oil in a mixture of acetic anhydride, chloroform and sulphuric acid are allowed to stand for 5 minutes, and then mixed with ethyl ether. Teaseed oil gives a magenta-red colour, the intensity of which is proportional to the amount of that oil present. Negative results are given by maize, cottonseed, arachis, sesame, sunflower, rapeseed, soya bean, poppy, mustard and olive oils. A faint pink colour may be developed in some instances with olive oil, but it cannot be confused with the characteristic colour given by teaseed oil.

The reliability of the Fitelson test has been demonstrated by experience in Government and State food control laboratories over a period of about a year. Since the test was available no official samples have been found to contain teaseed oil, but three unofficial samples of salad oils submitted by purchasers have shown substantial proportions of that oil.

"COLOUR ADDED" ORANGES.—The legend "colour added" now appears quite generally on Florida oranges. Trees that flower out of season produce what is known as "off-bloom" fruit, the colour of which is variable and not typical of the normal varietal production. Although the oranges may be fully matured and of normal palatability, there is a prejudice against them because the non-uniform natural colour creates an impression that the fruit is unripe and unpalatable. The State of Florida has therefore passed legislation permitting artificial colouring and regulating the practice. The Florida Citrus Commission specifies the requirements that must be met before the fruit may be coloured, and the Commissioner of Agriculture is charged with enforcing these requirements. One of the chief requirements is that no fruit that has not attained a satisfactory degree of ripeness shall be coloured. This condition is judged by the ratio of sugar to fruit acid, which must not be less than 8 to 1.

Under the statutes in Connecticut, artificial colouring of foods is not illegal, provided that the colour is harmless, and that the colouring does not conceal damage or inferiority. All the fruits examined had a sugar to acid ratio exceeding 8 to 1. In four unofficial samples the acidity and distribution of sugars were as follows:—Acidity (as anhydrous citric acid), 0·48 to 0·96 g. per 100 ml.; total sugars, 5·87 to 8·46; sugar to acid ratio, 8·9 to 12·2. One "colour added" sample was dyed with a colour which was not one of the permitted yellow shades; it closely resembled Sudan II.

VITAMIN *D* MILK.—Three methods of imparting vitamin *D* potency to milk are recognised by the Milk Regulation Board of Connecticut, namely, (1) direct irradiation of milk; (2) addition of a concentrate of cod-liver oil; (3) production of milk by cows fed with irradiated yeast. These products are sometimes referred to as "irradiated," "fortified" and "metabolised" milks, respectively. In June, 1935, the Milk Regulation Board charged the Dairy and Food Commissioner with the duty of a systematic inspection of these products offered for sale in the State.

Labelling regulations for vitamin *D* milk require only that the process of production be designated on the bottle cap. The regulations recognise the prevailing commercial practice for the three types of products, and the types are judged accordingly. Thus irradiated milk should contain not less than 135 units per quart; cod-liver oil concentrate milk (or milk fortified with activated ergosterol), 400 units; and milk produced by yeast feeding, 430 units. The relative nutritional efficacy of these different types and potencies is not clearly established at this time, but it is sufficient to say that all are effective for the prophylaxis of rickets.

In conducting the tests on market samples of vitamin *D* milk, the milk is fed to white rats which have been maintained, for about three weeks after weaning, on a diet that will cause them to develop a marked condition of rickets. The amount of milk fed varies according to the potency expected and required for the type of milk fed, and the vitamin *D* content or activity of the sample is judged by the degree of healing in the bones of the animals. Under these conditions, satisfactory healing (recalcification of the bones) should be produced by all three types of milk.

VINEGAR.—Section 2456 of the Connecticut General Statutes provides that no vinegar may be sold or offered for sale as cider vinegar if it is not produced wholly from the juice of apples. It also provides that no drug, or any hurtful or foreign substance, or any colouring matter, or any acid, may be added to vinegar; and that no vinegar may have an acidity of less than 4 per cent. by weight of acetic acid. Section 2457 provides that vinegar shall be labelled to show the kind or identity of the product. Regulations provide that natural vinegars may be diluted to legal strength of acidity if the fact of such dilution is declared; and that dilute acetic acid is not vinegar and may not be sold as such; but it may be sold under its correct name for food purposes if it is free from harmful impurities.

A vinegar may be made from any alcoholic liquid which is subjected to the action of the acetic-acid-forming organism, which organism is present in the so-called "mother-of-vinegar." Vinegars are named according to the source of the alcohol from which acetic acid is produced. Cider and wine vinegars are derived from the alcoholic and subsequent acetous fermentations of apple and grape juices, respectively. Malt or beer vinegar is made by similar fermentations of malted barley or other malted cereals. Similarly, glucose vinegar is derived from glucose solutions, and sugar vinegars from solutions of sugar refiners' syrup or molasses. Vinegar may also be made from distilled alcohol, and such is known as spirit vinegar, or distilled vinegar.

As distilled vinegar should contain little or no formic acid, and commercial acetic acid contains considerable amounts, a formic acid determination has been used to show the presence of diluted commercial acetic in vinegars. Formic acid in excess of 10 mg. per 100 ml. is enough to cause suspicion, at least, if the article is sold as cider vinegar. Cider vinegar itself may apparently yield some formic acid by the procedure employed. This determination is obviously of no value as a diagnostic measure when commercial acetic acid of the purer grade is used.

As the transformation of alcohol into acetic acid is likely to be incomplete in the process of making distilled vinegar, a determination of alcohol is helpful in indicating the source of acetic acid in suspected samples.

Pratolongo (*Ann. Chim. Applic.*, 1925, **15**, 72) suggested the determination of oxygen value and iodine value as a means of distinguishing between dilute acetic acid and distilled vinegar. Schmidt (*Z. Unters. Lebensm.*, **1935**, **69**, 472; Abst., ANALYST, **1935**, **60**, 705) pointed out the necessity of removing caramel before applying these tests. It was found, however, that the iodine values were not sufficiently distinctive to be of service. For example, distilled vinegar without caramel colour gave an iodine value of 23, and with caramel added a value of 24 was obtained. Dilute acetic acid without caramel gave an iodine value of 19, and with caramel a value of 23.

The oxygen value is somewhat more indicative, provided the values are low; if they approach those given by distilled vinegar, the conclusions are again uncertain. The oxygen value was determined as follows:

Take a quantity of vinegar sufficient to yield a solution of 3 per cent. acidity when diluted to 100 ml. To such quantity add 1 g. of "Norit," dilute to a volume of 100 ml. shake for 2 minutes and filter. Take 50 ml. of the filtrate, add 2 ml. of 1:1 H_2SO_4, heat just to boiling and titrate with $N/10$ $KMnO_4$ until the pink colour developed lasts for half a minute. The volume in ml. of $N/10$ $KMnO_4$ consumed, corrected for a blank determination made with distilled water carried through the same procedure, is the oxygen value of the vinegar.

The end-point is fugitive, except with uncoloured dilute acetic acid, and cannot be determined with the same degree of accuracy as in inorganic permanganate determinations.

Trials of distilled vinegar and dilute acetic acid showed values of about 5 for the former and zero for the latter. The method cannot be applied to cider vinegar because the end-point cannot be read to even approximate accuracy owing to the large amount of manganese dioxide formed. Cider vinegars give oxygen values well over 100.

In the examination of commercial vinegars, in only one instance did the oxygen value clearly point to the use of dilute commercial acetic acid. In several other instances the inspection evidence pointed in the same direction, but the oxygen values did not support that conclusion.

RUBBING ALCOHOL.—Alcohol for massage purposes should be grain alcohol rendered unfit for beverage purposes by the addition of suitable chemicals. Acetone, boric acid, diethylphthalate and zinc phenolsulphonate are commonly used as denaturants. Section 2674 of the Connecticut General Statutes makes the use of methyl (wood) alcohol in this and other toilet preparations unlawful.

Twenty-two samples were submitted by the Dairy and Food Commissioner. None of them contained methyl alcohol and no denaturants other than those mentioned were detected. The preparations were declared to contain not less than 70 per cent. of alcohol, and that amount was met or exceeded in all except three of the samples.

FLUID EXTRACT OF ERGOT.—The U.S.P. procedure requires assays of ergot preparations to be made by the cockscomb method. As the Station laboratory has no facilities for carrying out such a technique, a number of samples were examined by the chemical method discussed in *J. Assoc. Official Agr. Chem.*, **1933**, **16**, 387; **1934**, **17**, 453. The standard used was ergotoxine ethanesulphonate obtained through courtesy of the U.S.P. XI Revision Committee. This chemical procedure is supposed to give results comparable with those obtained by the cockscomb method. The U.S.P. XI standard is not less than 0·5 mg. of ergot alkaloids per ml. of fluid extract.

Eight samples of fluid extract, representing as many manufacturers, were tested, and the results ranged from 0·00 to 0·38 mg. per ml. Three preparations assayed 0·37 to 0·38; three others, 0·11 to 0·22; and two showed 0·005 and 0·00, respectively.

Since the official method of assay was not used, the products were not judged as to their compliance with U.S.P. requirements.

FRUITS OF WILD PLANTS.—Four samples of the fruits of wild plants, upon which birds and other forms of wild life feed, were examined, and the following results were obtained:

	Moisture		Ash		Protein*		Fibre		*N*-free extract		Crude fat (ether extract)	
	A Per Cent.	B Per Cent.	A Per Cent.	B Per Cent.	A Per Cent.	B Per Cent.	A Per Cent.	B Per Cent.	A Per Cent.	B Per Cent.	A Per Cent.	B Per Cent.
High bush cranberry ..	47·32	5·9	1·70	3·03	2·66	4·75	6·32	11·28	37·07	66·16	4·93	8·80
Japanese barberry ..	27·58	4·80	2·27	2·98	11·03	14·50	6·13	8·06	44·93	59·06	8·06	10·60
Red-berried nightshade	11·21	4·50	4·76	5·12	15·98	17·19	18·19	19·57	36·54	39·29	13·32	14·33
Ibota privet	24·14	2·83	2·73	3·50	8·49	10·88	9·13	11·70	44·66	57·19	10·85	13·90

A. As received. B. Air-dry material. * $N \times 6{\cdot}25$.

FOOD ADVERTISING.—In 1929 the American Medical Association established a Committee on Foods, "for the purpose of preventing or discouraging unwarranted incorrect or false advertising claims in the promotion of food products, and thus protecting the public and the medical profession against deception." The name of this Committee was subsequently changed to "Council on Foods." The Council works in harmony with federal agencies delegated to administer the Federal food law on misbranding, etc., and its scope is essentially in the field of collateral advertising involving "health" and nutritional claims. The work of this Council has been welcomed both by food manufacturers and advertising agencies, and many advertising programmes have been revised and brought into accord with its rules and regulations.

The Council has no authority to impose its decisions, but it grants manufacturers or distributors of food products authority to use its seal when all its requirements have been complied with. This seal is not a guarantee or recommendation of a product, but signifies that the product, its label and all advertising matter relating thereto have been considered by the Council and nothing contrary to its rules has been discovered.

A few of the conclusions adopted by the Council are as follows:

Good food advertising.—Proper food advertising should use the common name of the food concerned, or in the case of a fanciful trade name should identify the ingredients in the order of their decreasing proportions in the product. Such practice prevents deception. Any statement of the physical, chemical, nutritional or physiological properties and values of the food should be truthful and expressed in simple common terms. Proper advertising is free from false implications.

Food advertising claims with scientific or technical significance.—Statements or claims in food advertising with technical, scientific, nutritional, physiological or health significance shall be carefully phrased so as to be in complete accord with established knowledge and authoritative opinion, and shall be free from misleading or incorrect popular implications or interpretations.

Sleep-inducing claims for specific foods.—Sleep-inducing claims are not permissible for specific food beverages, because of their misleading character implying the possession of unique sleep-inducing properties by the specific individual foods, and because they lead to grossly deceptive advertising practices. No objection is taken to statements averring the relaxation value of hot drinks at bedtime for inducing sleep and accompanied by recommendation of the particular food drink for this purpose.

Mastication not an aid to health of teeth and gums.—Claims that the mastication of specific foods "keeps the teeth and gums clean and healthy," and equivalent statements, are meaningless, misleading and deceptive by implication and are not permissible.

Use of term "sterile."—The terms "sterile," "sterilised" and "sterilisation" shall be used in food advertising in their correct significance only. Foods processed to be free from pathogenic organisms or to keep sound and wholesome are not necessarily sterile, *i.e.* free from viable micro-organisms.

Tonic claims.—The term "tonic," or its inflected forms, have vague and misleading meanings or implications in food advertising and are not permissible.

Gelatin not an aid to the digestibility of milk.—There is no satisfactory evidence that gelatin increases the digestibility of milk or milk products. Such claims are not permissible.

Vitamin E claims.—Statements or claims referring to vitamin *E* in advertising to the public imply a need for special sources of the vitamin that is not warranted by present knowledge. Neither claims for vitamin *E* nor mention of the vitamin shall appear on food labels or in advertising.

Blood-building claims in advertising.—Anaemia is a condition in which the blood is deficient in haemoglobin. It may be due to an inadequate diet, but pathological conditions are frequently involved. Blood-building claims should be excluded from food advertising.

Acidosis claims.—The terms "acidosis," "acidity" and "acid" are frequently used in advertising, to play on vague fears of the public. Acidosis is a medical name for a morbid condition in the reserve supply of fixed alkali in the blood and body fluids. The term "acidosis" is so little understood by laymen that its use is misleading.

Whole wheat and Graham foods.—The terms "whole wheat," "entire wheat" and "Graham" as applied to flour and to bread are synonymous. In harmony with this understanding, these terms shall be used as food names, or as parts of food names, only when the sole cereal and farinaceous ingredient is whole wheat. Their use as names for foods with other composition is misinformative and misleading. Descriptive food names shall correctly and properly identify the nature of the foods.

"Resistance" claims in food advertising.—"Resistance" depends on many factors other than diet or any one dietary essential. Insufficiency of a dietary essential may eventually break down health; but more than is necessary of one or more of these essentials for adequate body reserves does not lead to a "super-resistance." "Resistance" produced by adequate nutrition is not to be confused with immunity resulting from antibodies in the body fluids produced by the body cells in their defensive reaction against pathogenic organisms and their toxins. Food advertising should conform to this established knowledge.

Medical Research Council

THE USE OF THE DEVELOPING EGG IN VIRUS RESEARCH*

THIS report deals with a method which has proved of much value in the study of human and animal diseases due to filter-passing viruses—a method which may come to have still greater importance in research work and in practical applications to prevention and treatment. The chorio-allantoic membrane of the developing chick was first used by Rous and Murphy in 1911 for studies of fowl tumours, and since then has been applied to tumours of other sources. In 1931 Goodpasture and Woodruff showed that this egg membrane was very suitable for the growth and study of a number of viruses. The technique was modified in 1933 by Burnet, who introduced the device of transferring the natural air-space from the butt end to the side of the egg, thus providing a relatively large area of susceptible membrane over which the virus can be spread. The success of the method is due to the chorio-allantoic membrane possessing the essential attributes of a living body, and to the fact that the resistance of the embryo is imperfectly developed, so that viruses to which chickens and fowls are immune multiply freely.

The list of viruses which can infect this membrane is so long and varied that it comes almost as a surprise to find that certain viruses cannot grow upon it. The technique is described in detail, the eggs must be fertile, and they must be given a preliminary incubation, usually of 12 days, before inoculation is made. A triangular window is cut in the shell on the side of the egg, the shell membrane is pierced with a needle, lifted from the chorio-allantoic membrane so that a small slit can be made in the former without damage to the latter. After inoculation a rim of paraffin-vaseline is built up round the triangle, a warm sterile coverslip is placed over the opening, the egg is re-incubated, usually for three days, and then examined.

Comparison of the effects of different viruses show remarkable specificity; some viruses, such as vaccinia and psittacosis, produce lesions mainly on the membrane, others (*e.g.* fowl plague and vesicular stomatitis) kill the embryo before characteristic foci on the membrane develop, others, again, such as louping ill and the influenza viruses, produce both local lesions and general effects on the embryo, whilst the viruses of foot and mouth disease, poliomyelitis and rabies have no effect at all.

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* Medical Research Council Special Report Series, No. 220. By F. M. Burnet.

By means of the developing egg (1) quantities of bacteria-free virus-containing material can be obtained for experimental work or for immunisation; (2) with suitable viruses it is a satisfactory experimental animal for virus titrations in the case of lethal viruses by determination of the minimum quantity causing death of the embryo and therefore containing at least one virus particle, or in the case of pock-producing non-lethal viruses by noting the number of specific foci produced by a known volume; (3) the study of the virus inactivating properties of immune sera can be made upon it, the inoculation of virus + immune serum being without effect. (4) In certain instances the method can be used as a diagnostic agent, as in differentiating foot and mouth disease and vesicular stomatitis; and (5) by the facility it offers for the propagation of such host-specific viruses as human influenza and mouse ectromelia it should be of value in investigating any infectious disease of unknown aetiology.

It is of interest to note that with the influenza virus the membrane lesions, almost unrecognisable at first, increased in size with egg-passage, and that from the 50th passage titration by pock counting could be made; after the 52nd passage there were indications of harmful effects on the embryos which died between the 4th or 5th day. The time of death was progressively earlier with further passage, and embryos have been found dead in 44 hours at the 76th passage. The virulence of the egg passage strain for ferrets fell so far as to produce a slight rise in temperature only in two out of five as the only manifesting symptoms, yet this virus immunised the ferrets solidly against virulent virus. This loss of virulence with retention of immunising power suggests the possibility of producing on the same lines an innocuous virus which may be used to confer immunity on human beings by intra-nasal administration. D. R. W.

British Standards Institution

BRITISH STANDARD SPECIFICATION FOR DENSITY BOTTLES

A SPECIFICATION for Density Bottles (B.S.S. No. 733—1937)* has been issued by the British Standards Institution, and is intended to complete the series of specifications relating to methods of determining the density of a liquid. The specification for Density Hydrometers was recently issued (*cf.* ANALYST, 1937, 129).

The capacity of a density bottle, standard at 20° C., is defined by the volume of water of temperature 20° C., expressed in millilitres, required to fill the bottle at 20° C.

Part II of the present specification gives precise details for determining the weight of liquid required to fill the bottle at 20° C., and thence the weight of liquid occupying unit volume at 20° C. From this the density—mass per unit volume—of the liquid at 20° C. in grams, per millilitre, is obtained by adding a small buoyancy correction. Directions are also given for obtaining the density at a temperature (t° C.) other than 20° C.

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[*] Copies of these Specifications may be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d.

BRITISH STANDARD SIZES FOR PAPER

(WRITINGS AND PRINTINGS, WRAPPINGS AND CASINGS, AND TRIMMED BOARDS)

B.S.I. SPECIFICATION, No. 730—1937.* (*Approved by the Chemical Divisional Council, and published under the authority of the General Council, April 12th,* 1937.)

The list of British Standard sizes for paper given in this specification has been prepared at the request of the Australian Standards Association with a view to its adoption ultimately as a British Empire Standard list of sizes. The Committee appointed prepared a list of sizes based very largely on the work carried out several years ago by the Federation of Master Printers and Allied Trades of the United Kingdom of Great Britain and Ireland, and this list was given a very wide circulation, both in the Dominions and in this country, for one year.

In considering the comments received, the Committee has ruled out any proposal which involved more than one size for one name, as being contrary to the interests of industry. The British Standard list of sizes now issued covers the sizes used in this country and the Overseas Dominions, with the exception of India. With regard to Canada, they lean towards the sizes common in the United States. As the Indian sizes differ somewhat, the Indian authorities have been invited to go into the matter in detail with the object of a review in two years' time, when it is hoped it may be possible to obtain agreement to the recognition of the list as a British Empire Standard. In the meantime the Committee is recommending that Australia, South Africa and New Zealand issue the list as their own local standard during these two years.

Appendix A tabulates certain sizes in which official and other publications have been issued for a great number of years. They can only be obtained if a sufficiently large order justifies their being made.

Appendix B deals with the possibility of issuing recommendations with regard to the standardisation of listing and invoicing weight and stating substance. As various sections of industry differ in their views on these points, no specific recommendations are made, but it is suggested that, for writing and printing papers, the following system may eventually prove suitable for adoption. It is used at present by H.M. Stationery Office, and has the approval of the Federation of Master Printers. Consideration of the system is invited with a view to its adoption in two years' time.

(1) *Listing and invoicing weight.*—That the method of listing and invoicing paper in terms of weight, in pounds, should be per 1000 sheets for paper and per 100 boards.

(2) *Packing.*—That paper should be packed in 500 sheets and boards in 100's.

(3) *Indication of substance.*—That the substance of paper and boards should be indicated in terms of grams per square metre, and that the substance as well as the weight should be shown on all packages, the weight of 1000 sheets being exclusive of wrapper and string.

NOTE.—The substance of a paper has in the past been stated in terms of weight of a ream of 500 sheets (or other quantity, *e.g.* 472, 480, 504, 508, 512 or 516 sheets) of the size concerned, the stated weights of paper similar in substance varying directly in relation to the area of the sheets and the number of sheets in the ream.

In order to have a simple method of making comparisons with regard to substance, no matter what the size of the paper or the number of sheets in the package, a system of symbols has been adopted and is in use by H.M. Stationery Office, by means of which immediate comparisons can be made. In terms of grams per square metre (a system similar to that in use in some Continental countries) a simple method is afforded for the convenience of both the supplier and the user. This is preferable to a system of substance numbers based upon the weight of a package or other quantity of each size of paper. The weight of 1000 sheets must be in accordance with that of the specified substance expressed as grams per square metre of the paper, excluding wrapper and string. For instance, in the case of demy, 17½ × 22½ in.—100 grams per square metre = 56 lb. per 1000 sheets.

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* Copies of these Specifications may be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d.

International Union of Chemistry

THE CLASSIFICATION OF QUALITATIVE ANALYTICAL REACTIONS

THE Committee* appointed by the International Union of Chemistry for the study of new analytical reagents, which made a critical examination of existing data on the sensitivity (limit of identification) and selectivity of tests of identity, at its meeting in Paris, May, 1937, has decided to distinguish between *specific* and *selective* reactions (and reagents) and recommends this convention for general use. Reactions (and reagents), which under the experimental conditions employed are indicative of one substance (or ion) only, are designated as *specific*, whilst those reactions (and reagents) which are characteristic of a comparatively small number of substances are classified as *selective*. From this it follows that it is permissible to describe reactions (or reagents) as having varying degrees of selectivity; on the other hand, a reaction (or reagent) can be only specific or not specific.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection and Estimation of Raw Milk in Pasteurised Milk by the Orla-Jensen Method. F. Stoppel. (*Z. Unters. Lebensm.*, 1937, 73, 327–329.)—The "creamometric" method of Orla-Jensen (*Z. Unters. Lebensm.*, 1932, 63, 300; Abst., ANALYST, 1932, 57, 383) is modified to enable it to indicate the presence of small amounts of raw milk in pasteurised milk. The amount of sample taken is increased six times and is diluted to four times its original volume, instead of twice, and the time allowed for separation of the cream is increased to 20 hours. The dimensions of the apparatus are correspondingly modified. The procedure is as follows:—The milk (30 ml.) is heated for 5 minutes at 50° C. in a 100-ml. flask and then quickly cooled. The flask is completely filled with water and connected by means of a piece of rubber tubing, about 5 cm. long, with the lower end of a Hoyberg butyrometer tube also filled with water. The connection should be perfectly water-tight, but the inclusion of a small bubble of air (about 1 ml.) facilitates mixing. The apparatus is inverted several times until the contents (120 ml.) are thoroughly mixed. The apparatus is then allowed to stand at a temperature of 12 to 15° C., for 20 hours, after which the depth of the cream layer in the butyrometer is read. The factor C of Orla-Jensen (*loc. cit.*) is calculated by multiplying the depth of the cream layer by 4 (the dilution), and dividing by the fat-content of the undiluted milk. The factor A of Orla-Jensen, being of less importance for the purpose of this determination, is not determined. When amounts of 5, 10, 15, 20 and 30 per cent. of raw milk were added to a pasteurised milk of fat-content 3·0 and original C-value 3·3, the C-value was altered to 8·0, 27·0, 33·3 and 53·0, respectively. The average values of the factor C for additions of 0, 5, 10, 15, 20 and 30 per cent. of raw milk (the ranges being given in brackets) are:—2·8 (2·0 to 4·0), 6·0 (4·0 to 9·3), 16·4 (3·9 to 22·7), 28·8 (22·7 to 34·0), 41·1 (32·0 to 47·0) and 55·9 (47·4 to 64·0). The advantages of the method are its convenience, the absence of chemical operations, and the absence of the personal error associated with methods depending upon colorimetric or, turbidimetric determinations. A. O. J.

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* W. Böttger (Leipzig), F. Feigl (Vienna), A. S. Komarovsky (Odessa), C. J. Van Nieuwenburg (Delft), N. Strafford (Manchester).

Bromine in Argentine Flours and Wheats. J. Viggiano and E. F. H. Türk. (*Anal. Assoc. Quim. Argentina*, 1936, **24**, 131–134.)—The method used for determining bromine in flours and wheats was as follows:—Ten g. of the finely-ground sample are mixed in a platinum or nickel crucible with water and 5 ml. of 10 per cent. sodium carbonate solution, and the mixture is heated over a small flame until carbonised. The residue is ashed at dull red heat in a muffle furnace; it is important to obtain a carbon-free ash, as otherwise negative results are obtained with small quantities of bromine. The residue is taken up in 10 ml. of boiling water and filtered. Five ml. of the filtrate are acidified with conc. sulphuric acid (6 drops) and the Denigès–Chelle reaction is applied by adding 4 drops of conc. hydrochloric acid, 4 drops of a 10 per cent. potassium chromate solution, and 1 ml. of conc. sulphuric acid and mixing. The liquid is cooled in water for at least 5 minutes, treated with 1 ml. of sulphuric magenta reagent (prepared by adding 10 ml. of a freshly-made 0·1 per cent. solution of basic fuchsin to 100 ml. of dilute (1 : 20) sulphuric acid) and 1 ml. of chloroform (washed with water to remove traces of alcohol), and shaken vigorously for 1 minute. A violet colour in the chloroform layer indicates the presence of bromine. The bromine is estimated by comparing this colour with a series of standards prepared by the above-described method from a potassium bromide solution, 1 ml. of which is equivalent to 0·0125 mg. of bromine (0·0186 g. of potassium bromide per litre) (Chelle and Vitte, *Ann. Falsif.*, 1936, **29**, 98; Abst., ANALYST, 1936, **61**, 343). A blank reaction is carried out. The following experimental results are given:

	Bromine		
Region from which the wheat was obtained	Whole wheat mg. per kg.	Flour mg. per kg.	Bran mg. per kg.
Basavilbaso	6	4	6
Necochea	2·5	2·5	2
Córdoba	6	5	6
Tandil	4	4	4
Lincoln	4·5	2·5	4
Concordia	6	4·5	7
Tres Arroyos ..	2·5	3·5	2·5
San Francisco ..	4	4·5	4
Agustina, F.C.P. ..	2	2	2
Chacabuco, F.C.P. ..	2	2	2·5
Average ..	3·95	3·45	4·00

E. M. P.

Extraction and Preliminary Examination of Various Coloured Compounds in Red Wines. A. Dangoumau and G. Debordes. (*Bull. Soc. Chim.*, 1937, **4**, 910–911.)—Fifty ml. of red wine were extracted continuously with ether for 8 days, during which time the original liquid diminished in volume to about 3 ml. of a deep red liquid soluble in water. Ether did not extract the colour from this liquid, whilst alcohol removed part of it. The alcoholic and aqueous fractions were examined spectrographically, the spectra being identical with that of the original wine. After long standing, the extract formed two layers, the ethereal layer being bright yellow. The experiment was repeated, 150 ml. of the wine being extracted with ether. After distillation of the solvent there was left a brick-yellow substance soluble in ether. Petroleum spirit did not extract colouring matters from small quantities of wine, but removed a yellow substance from large quantities. E. M. P.

Identification of Wine Vinegar. A. Schmidt. (*Z. Unters. Lebensm.*, **1937, 73,** 441–447.)—As described previously (*Z. Unters. Lebensm.*, 1935, **69**, 472; Abst., ANALYST, **1935, 60,** 705) the "oxidation value" of wine vinegar is the number of ml. of *N*/10 potassium permanganate solution required to impart a red colour persisting for 2 minutes to 50 ml. of vinegar acidified with sulphuric acid. For wine the value is 50 or more, whilst for wine vinegar of acidity 9·2 to 9·4 per cent. the value is about 30, and for wine vinegar of 3 per cent. strength it varies from 8 to 12. The iodine value (Schmidt, *loc. cit.*) is determined by adding excess of *N*/100 iodine solution to 25 ml. of vinegar which has been made alkaline, allowing the mixture to stand for 15 minutes, acidifying with hydrochloric acid, and titrating the excess of iodine with *N*/100 sodium thiosulphate solution. With concentrated wine vinegar about 400 ml. of *N*/100 iodine solution must be used, since the iodine value is extraordinarily high, and for wine vinegar of acidity 3 per cent. 150 ml. are required to provide the necessary 25 per cent. excess of iodine solution. The iodine value of wine is 150 to 250, that of concentrated wine vinegar about 300, and that of the weaker wine vinegar 90 to 100. No other form of vinegar has so high a value. Since the iodine value of wine vinegar is about double that of the wine from which it is prepared, it follows that substances absorbing iodine are formed during the acetic fermentation. The author has previously stated that the difference between the iodine values of wine and spirit vinegars is small. This statement, based upon the examination of a few unauthenticated commercial samples, is now found to be erroneous and, by the investigation of a number of fully authenticated samples of wine vinegar, the iodine value is shown to be a very important distinguishing character. The determination must not be carried out by the method of Pratolongo (*Ann. Falsif.*, **1933, 37**), which involves distillation, because not all the substances reacting with iodine are volatile. Acetylmethylcarbinol, $CH_3COCH(OH)CH_3$, present in wine vinegar, is formed during acetic fermentation by the condensation of two molecules of acetaldehyde brought about by the enzyme carboligase. It may be detected by conversion into diacetyl which, in turn, may be converted into nickel dimethylglyoxime, but the simplest method for its detection and determination is a modification of that of Arbenz and Pritzker (*Mitt. Lebensmittelunters.*, **1931, 22,** 354) depending upon its power of reducing cold Fehling's solution. The cuprous oxide so formed is transferred to a narrow centrifuge tube, in which it is washed by centrifuging with water, alcohol and ether, dried at 30 to 40° C., and weighed.

The smallest amount found in wine vinegar of 3 per cent. acidity was about 60 mg. per litre; in wine vinegar of 9 per cent. acidity it reached 190 mg. per litre. In a mixture of equal parts of wine and spirit vinegars the amount found was 38 mg. per litre and, since acetylmethylcarbinol does not occur in spirit vinegar, the same result would have been obtained if the diluent had been water. The minimum values suggested for wine vinegar of strength corresponding with 3 per cent. of acetic acid are:—oxidation value, 8 ml. of $N/10$ potassium permanganate solution; iodine value, 90 ml. of $N/100$ iodine solution; acetylmethylcarbinol-content, 60 mg. per litre. The values found for samples of wine vinegar of strength corresponding with 9 per cent. of acetic acid were:—oxidation value, 30 to over 40; iodine value, 240 to 300; acetylmethylcarbinol-content, 140 to 193. The acetylmethylcarbinol-content is particularly useful for the detection of the adulteration of wine vinegar with spirit vinegar. The glycerol-content and the extract of wine vinegar vary considerably, and the ester value does not serve as a useful criterion.

A. O. J.

Detection of Oils derived from the *Cruciferae* in Edible Oils. J. Grossfeld. (*Z. Unters. Lebensm.*, 1937, **73**, 409–426.)—Methods depending upon the separation of erucic acid (Holde and Marcusson, Abst., ANALYST, 1910, **35**, 401; Thomas and Mattikow, *J. Amer. Chem. Soc.*, 1926, **48**, 968; Täufel and Bauschinger, *Z. angew. Chem.*, 1928, **41**, 157; Kimura, Abst., ANALYST, 1930, **55**, 645; Bertram, *Z. Unters. Lebensm.*, 1928, **55**, 179) have the disadvantage that the separation is tedious and difficult. Tortelli and Fortini (Abst., ANALYST, 1910, **35**, 401) used the iodine value of the solid fatty acids which give lead salts insoluble in ether. Kreis and Roth (Abst., ANALYST, 1913, **38**, 434) used fractional precipitation of the fatty acids as lead salts. The resemblance of erucic acid to iso-oleic acid in its behaviour suggested that a modification of the method of Grossfeld and Peter (*Z. Unters. Lebensm.*, 1934, **68**, 348; Abst., ANALYST, 1935, **60** 105) for the detection of hardened fats could be applied to the detection of rape oil in other edible oils. The modification consists in the addition, to the oil, of lauric acid, which has the effect of promoting crystallisation, bringing down the erucic acid by adsorption, and compensating for the differences in vegetable oils caused by variations in the content of individual saturated and unsaturated acids. The "erucic acid value" is determined as follows:—About 500 mg. of the oil and 0·6 ml. (500 mg.) of melted lauric acid are saponified beneath a reflux condenser for 10 minutes with 10 ml. of alcoholic potassium hydroxide solution (40 ml. of potassium hydroxide solution of sp.gr. 1·5 with 40 ml. of water made up to 1 litre with 96 per cent. alcohol). To the cooled soap solution are added 50 ml. of lead acetate solution (5 g. of crystalline lead acetate and 5 ml. of 96 per cent. acetic acid made up to 1 litre with 80 per cent. by vol. alcohol), 2·5 ml. of 95 per cent. acetic acid and 10 ml. of water. The mixture is heated beneath a reflux condenser until the lead salts have dissolved, then cooled, and allowed to stand at 20° C. in a stoppered flask, with occasional shaking, for 2 or 3 days. The deposit is filtered off in a sintered glass crucible (Schott und Gen. 10G/3), and washed with 10 to 15 ml. of 70 per cent. alcohol. The crucible is placed in a continuous extractor and extracted with a mixture of equal parts of 96 per cent. alcohol and 96 per cent. acetic acid. The warm solution of the lead salts is rinsed into a 400-ml. flask with 10 ml. of the alcohol and acetic acid mixture, and the iodine absorption is determined by the method of Margosches, Hinner and Friedmann (*Z. angew. Chem.*, 1924, 37, 334). For this purpose, 20 ml. of alcoholic 0·2 *N* iodine solution are added, the mixture is well shaken and diluted with 200 ml. of water and, within two hours of the dilution, the excess of iodine is titrated with *N*/10 sodium thiosulphate solution. A blank determination is made upon 30 ml. of the alcohol and acetic acid mixture. The number of ml. of *N*/10 iodine absorbed is the "erucic acid value." By applying the method to known mixtures of olive oil and erucic acid it was found that the relation between the weight of erucic acid in mg. (y) and the erucic acid value (x) is given by the equation $y = 52{\cdot}1x - 0{\cdot}9x^2 - 217{\cdot}2$. Since x is 4·52 when y is 0, titrations of less than 5 ml. are ignored. By comparison of the actual with the calculated values it is found that the erucic acid is determined with an accuracy of ± 11 mg., corresponding with 2·2 per cent. of rape oil. The erucic acid value of pure rape oil is about 12, corresponding with 54 per cent. of erucic acid. A. O. J.

Characterisation of the Acetyl Group in some Medicaments by means of "Lanthanum Blue." A. D. del Boca and A. L. Remezzano. (*Quim. e Ind.*, 1937, 14, 195–197.)—The formation of a blue adsorption compound of iodine on basic lanthanum acetate is used as a test for the acetyl group. To 1 ml. of the liquid under examination is added 1 ml. of 5 per cent. lanthanum nitrate solution, 1 ml. of *N*/50 iodine solution, and *N* ammonia until the liquid is pale yellow. In the presence of an acetate a blue colour appears in the cold, and there forms a gelatinous precipitate; with small quantities of acetate the colour is violet and appears on warming. The test is not affected by nitrates, chlorides, bromides, or iodides, but phosphates and sulphates must be removed. Oxalates and formates are destroyed during the preliminary distillation (see below), while other organic acids can be separated by distillation. Propionic acid behaves in the same way as acetic acid, and butyric and valerianic acids invalidate the test. The reaction has been applied to heroin, aconitine, aspirin, tannigen, acetanilide, antifebrin and salophen, the following methods being recommended:

Heroin and Aconitine.—A quantity of 0·01 to 0·02 g. of the alkaloid is distilled from a 50-ml. flask with 2 to 3 ml. of 50 per cent. sulphuric acid; half the quantity of liquid is distilled over. Four or 5 drops of the distillate are added to a 5 per cent. lanthanum nitrate solution, and the mixture is treated with *N*/50 iodine solution and *N* ammonia. With small quantities of acetate a ring test should be made, the ammonia being run in down the side of the tube.

Aspirin and Tannigen.—The hydrolysis is carried out with ferric chloride instead of sulphuric acid, the technique being as follows:—A quantity of 0·01 to 0·02 g. of the material is distilled gently with 2 or 3 ml. of 30 per cent. ferric chloride solution until about 2 ml. of distillate have been obtained; the test is applied to this.

Antifebrin, Exalgin, Phenacetin and Salophen.—The procedure described for heroin and aconitine was used; the first three gave positive results, but salophen gave a negative result. E. M. P.

Fluorine-content of Gelatin. L. S. Stuart, D. Dahle and R. W. Frey. (*J. Amer. Leather Trades Chem.*, 1937, 205–210.)—The fluorine-content of samples of commercial gelatin of German, American and British origin was found to range from 4 to 10 p.p.m. The fluorine-content of gelatin made from calfskin cured with salt to which fluorides had been added varied according to the manner in which the skin was washed prior to liming. With thorough washing in running water these gelatins had about the same fluorine-content as gelatin cured with salt alone or as commercial gelatin. Skins washed by still soaking contained more fluorine. It was concluded that an increased fluorine-content of gelatin made from calfskin cured with salt plus fluorides may result from the use of commercial salt containing impurities capable of forming difficultly soluble fluorides, and also from lime containing fluorine used for the purpose of de-hairing. The method recommended for fluorine determination involves separation by a single distillation by Willard and Winter's method (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7; Abst., ANALYST, 1933, **58**, 242), followed by its determination in the distillate by the peroxide and titanium method (Wichman and Dahle, *J. Assoc. Off. Agr. Chem.*, 1933, **16**, 612; Abst., ANALYST, 1934, **59**, 132). S. G. C.

Commercial Thyme. C. E. Sage. (*Perf. and Essent. Oil Record*, 1937, **28**, 127–128.)—In order to elucidate the very different aroma, which has been more pronounced in recent years, between French and English thyme (*Thymus vulgaris*), seed found in a consignment of imported thyme leaf was germinated, and it was confirmed that the resulting plants, grown in England, were *T. vulgaris.* It is suggested that the difference in scent between foreign and English-grown thyme is analogous to that found in Surrey peppermint grown in this country and in America. The difference would appear to be due to climate. Thyme of Spanish origin may show considerable differences in scent, but this is usually due to the fact that different species often grow side by side, and these contain varying amounts of carvacrol, thymol and citral. Analyses of 15 samples of commercial shipments of dried thyme leaves showed the following variations:—total ash, 6·64 to 13·82 per cent.; acid-insoluble ash, 0·83 to 5·80; essential oil, 0·64 to 1·84 per cent., and $n_D^{20°}$ of the oil 1·491 to 1·512. Traces of arsenic (not usually above 1/100th of a grain per lb.) may be present in dried thyme, and for culinary purposes it is important to free the herb from grit. D. G. H.

Chemical Examination of *Clerodendron infortunatum*. Part I. H. N. Banerjee. (*J. Indian Chem. Soc.*, 1937, **14**, 51–57.)—*Clerodendron infortunatum*, the Indian Bhant or Bhat (N.O. *Verbenaceae*) is a shrub common throughout the warm regions of India from Gurhwal and Assam to Ceylon. The young twigs, ground to a paste and made into pills, are used for the destruction of intestinal worms. A sample of the dried leaf had the following composition:—ash, 8·04; protein, 21·12; crude fibre, 14·84; free reducing sugars, 3·00; and total sugars (after inversion), 17·05 per cent. The air-dried, finely powdered leaves were treated with Prollius fluid, but no alkaloids were found. Extracts of the dried leaf were made with various solvents, and petroleum spirit was found to dissolve 3·85 per cent., giving a deep greenish-yellow, very bitter solution. On concentration, crystals were formed, and these, when re-crystallised from boiling

50 per cent. alcohol, yielded long needles melting at 161 to 162° C., and having a very bitter taste. On steam-distillation of the green pasty residue from the petroleum spirit extract a volatile oil with a strong odour of the drug was obtained. By repeated extractions with 60 per cent. alcohol a further crop of crystals of the bitter substance, to which the name *clerodin* was given, was obtained, the total yield being 0·12 per cent. of the air-dried leaf. After complete removal of the clerodin, and by repeated extraction of the pasty mass with 80 per cent. alcohol, crystals of a sterol were obtained. The dark residue was decolorised in ethereal solution by means of charcoal and fuller's earth, and saponified, the soap was dissolved in water, and the free fatty acids liberated and purified. The "liquid" acids (80 per cent.) consisted of oleic 74·9, and linolenic 25·1 per cent., and the "solid" acids (20 per cent.) of stearic, 48·8, and lignoceric acid, 51·2 per cent. Carotene and xanthophyll were separated from the unsaponifiable matter. The sterols comprised 1·20 per cent. of the oil, and hydrocarbons appeared to be almost absent from the residual unsaponifiable matter, which seemed to consist mainly of aliphatic alcohols. Varying amounts of clerodin were found in different parts of the plant; young leaves and twigs collected before rains contained 0·12 per cent.; just after rains 0·55 per cent.; in old leaves there was 0·05 per cent., and in stems and roots only traces were found. Clerodin had no haemolytic action on human red blood corpuscles, nor had it any bactericidal properties when tested against *B. coli*. The toxicity to earthworms was tested by Sollman's method (*J. Pharm. Exp. Therap.*, 1918, **12**, 129), and the clerodin killed them in aqueous solution within half-an-hour. The toxicity of drugs to earthworms is taken to be more or less parallel to their toxicity to parasitic worms, according to Straub and Tradelenberg, and drugs toxic to earthworms are regarded as possessing possibilities as anthelmintics. Small fish and mosquito larvae were killed in 30 minutes and 2 hours, respectively (Fink and Haller's method, *J. Econ. Entom.*, 1936, **29**, 595), so that clerodin is to be regarded as toxic to the lower forms of life. It was quite harmless to a rabbit fed with 0·1 g. dissolved in 10 ml. of olive oil. Clerodin is soluble in hydrochloric acid, olive and castor oils and glycerol, and slightly so in paraffin oil and vaseline. D. G. H.

Histology of *Podophyllum*. T. E. Wallis and S. Goldberg. (*Quart. J. Pharm.*, 1937, **10**, 40–51.)—This is a detailed account of the histology of *Podophyllum peltatum*, and is to be followed by a similar account of *P. emodi*. Measurements are given for the extreme range, as well as for the average values, of the dimensions of the important cells in each part of the drug. The important features to be sought for in the powder of American podophyllum (*P. peltatum*) are the brown epidermal cells, which are mostly elongated rectangular prisms, and usually 4 to 10 times as long as they are wide. In addition, a small number of similar cells, which are approximately isodiametric, are present, and all of these contain a dark red-brown material containing tannin. Cluster crystals of calcium oxalate are also present, and many of these exceed 60μ in diameter. Starch grains, ranging from 2 to 30μ in diameter and having an average value of 15μ, should also be seen.

S. G. S.

Biochemical

Reactions of Amino and Imino Acids with Formaldehyde. M. Levy and D. E. Silberman. (*J. Biol. Chem.*, 1937, **118**, 723–734.)—Further data are given for the reaction of formaldehyde with amino and imino acids. (See also *J. Biol. Chem.*, 1932, **99**, 767; 1934, **105**, 157; 1935, **109**, 365.) The method consisted in the determination of the variation in the apparent dissociation constants of the amino and imino groups with the formaldehyde concentration. The substances reported on are *dl*-alanine, *dl*-valine, *l*-aspartic acid, *l*-tryptophane, *dl*-sarcosine and *l*-hydroxyproline. The results indicate that amino acids may react with one or two molecules of formaldehyde, whereas imino acids can react only with one. The reaction of asparagine with formaldehyde is interesting in that a pyrimidine derivative is formed, but the rate of the reaction is very slow. As a result of this difference between asparagine and other amino acids it is concluded that the usual conception of methylene amino formation is incorrect, and other possibilities are discussed. S. G. S.

Determination of Lactic Acid in the Presence of Methylglyoxal. E. Bauer and F. Ziegler. (*Hoppe-Seyler's Z. phys. Chem.*, 1937, **247**, 1–5.)—In the determination of lactic acid, trouble from interfering substances such as methylglyoxal is frequently encountered. Several workers have suggested different methods for the elimination of these substances, but no method has been really satisfactory. The authors claim that oxidation with hydrogen peroxide in an acid medium prior to the distillation removes the methylglyoxal without affecting the lactic acid. The modified apparatus and manganese sulphate and sulphuric acid mixture of Fürth and Charnass was used with tenfold excess of hydrogen peroxide. Protein in the solution under examination interferes with the method and requires removal with sodium tungstate solution. Five ml. of $N/5$ phosphate buffer and 10 ml. of 10 per cent. sulphuric acid are added to the necessary amount of the solution under examination in a 50-ml. flask, and the whole is treated with 5 ml. of a 10 per cent. solution of sodium tungstate. The volume is adjusted to 50 ml., and the precipitate is removed by centrifuging or by filtration. Forty ml. of the filtrate (4/5 of the original) are pipetted into the distillation flask, and to this is added 10 ml. of the manganese sulphate and sulphuric acid mixture, 10 ml. of water and 0·2 ml. of perhydrol. Broken porcelain is added, and the whole is heated and kept gently boiling for 6 minutes. To remove excess of hydrogen peroxide potassium permanganate solution is added until a permanent pink colour is obtained, and the usual distillation is then carried out. In the absence of protein the test solution is oxidised without previous treatment with sodium tungstate. S. G. S.

Properties of Ricin. S. Inoue. (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 122–123B.)—Ricin was prepared by separating the oil from the flour of *Ricinus communis* L. and extracting the residue with a 10 per cent. solution of sodium chloride at 25° to 30° C. Globulin was then removed by dialysis for 4 days, and the filtered solution was saturated with ammonium sulphate; this caused a bright brown substance to separate, and an aqueous solution of this was dialysed in running water until no more sulphate ions were removed. The solution was evaporated under a reduced pressure at 40° C., a yield of 2·5 per cent. of ricin protein being obtained. This was shown to be an ampholytic hydrophilic colloid soluble in water or dilute sodium chloride solution, solutions in water being coagulated by heat or by addition of alcohol. It gave positive reactions with the biuret, Millon, xanthoprotein, ninhydrin, lead sulphide, Adamkiewicz, glyoxylic acid and diazo reagents for proteins, and a normal sample contained 16·81, 4·63 and 8·66 per cent. of total nitrogen and nitrogen coagulated by heat and tannin, respectively. The isoelectric point was determined by measuring the degree of turbidity produced on adding alcohol to solutions of ricin buffered at *p*H 4·5 to 9·0, and it was found to be 5·4 to 5·6. Examination under the ultra-microscope indicated that the mechanism of the coagulation of blood corpuscles by ricin is associated with the coagulation of ricin itself. The rate of coagulation was measured by adding 0·1 to 1·0 ml. of ricin to 1 ml. of blood at *p*H values ranging from 4·6 to 10·0, and it was shown that coagulation occurs only between *p*H 5·6 and 5·8 and between 8·9 and 9·1 It is therefore concluded that the so-called toxicity of ricin is mainly a colloidal phenomenon, and that determinations of such toxicity are valueless unless reference is made to the *p*H value. J. G.

Estimation of Total Vitamin *C* in Foodstuffs. P. N. Sen-Gupta and B. C. Guha. (*J. Indian Chem. Soc.*, 1937, **14**, 95–102.)—The following methods have been investigated: (1) treatment with trichloroacetic acid, (2) leaving in contact with trichloroacetic or hydrochloric acid, (3) heating in carbon dioxide or nitrogen for different periods, (4) treatment with hydrogen sulphide in the cold, and (5) treatment with hydrogen sulphide in the hot condition. The last method gave the highest value for ascorbic acid, and appears to give the total amount present, comprising the free vitamin, the ascorbic acid which is released by heating and the reversibly oxidised ascorbic acid. The possibility of this treatment releasing some non-specific reducing substance is guarded against by the addition of formaldehyde to the dye. This method is carried out by cutting 10 g. of the material into small pieces, and adding it to 50 ml. of water. Hydrogen sulphide is passed into this solution for 30 to 60 minutes, and, while the gas is still bubbling through the liquid, the whole is heated for 15 minutes on a boiling water-bath under a reflux condenser. The hydrogen sulphide is then removed by means of a current of carbon dioxide or nitrogen, and the suspension is treated with 2·5 ml. of a 20 per cent. solution of trichloroacetic acid. The mixture is filtered or centrifuged, and the filtrate is made up to 100 ml. This solution is used for the titration of 0·5 ml. of *M*/10 2:6-dichlorophenolindophenol solution to which 1 ml. of *M* formaldehyde and 1 ml. of glacial acetic acid have been added. The titration should be completed within one minute. S. G. S.

Vitamin *C* in Vegetables. Critical Investigation of the Tillmans Method for the Determination of Ascorbic Acid. G. L. Mack and D. K. Tressler. (*J. Biol. Chem.*, 1937, **118**, 735–742.)—The extraction of ascorbic acid from vegetables has been carried out by substituting a strongly ionised acid for the more usual acetic or trichloroacetic acid of the Tillmans method. It is claimed that with the lowered *p*H value, oxidation does not take place, and if, in addition, metaphosphoric acid is added, the inactivating effect of copper is eliminated. Sulphuric acid of strengths ranging from 5 to 15 per cent. is advocated, and it is also probable that hydrochloric acid may be equally successful. The use of these mineral acids eliminates the hydrogen sulphide treatment for all but exploratory work, and this greatly simplifies the procedure. Substances other than dehydroascorbic acid may be reduced by prolonged hydrogen sulphide treatment, and the strongly ionised acid prevents the interfering material from reacting with the titration reagent. The apparent increase in ascorbic acid on heating an aqueous extract, such as that from cabbage, is ascribed to the decomposition of the dehydroascorbic acid. S. G. S.

Estimation of Vitamin B_1. A. Schultz, L. Atkin and C. N. Frey. (*J. Amer. Chem. Soc.*, 1937, 59, 948–949.)—Determinations were made of the volume of carbon dioxide liberated in 3 hours by the fermentation of dextrose in the presence of various known amounts of vitamin B_1. For each test, 1 g. of yeast and 100 ml. of an aqueous solution containing synthetic salt mixture, buffer, and 3 g. of Merck's dextrose were used. The temperature was 30° C., and the oscillations were 100 per minute. Results with Merck's natural crystalline vitamin B were:

Merck's natural crystalline vitamin B_1 mg.	Ml. of gas in 3 hours
None	185
0·001	215
0·005	305
0·010	350
0·040	395
0·100	405

Determinations of vitamin B_1 based on these results and on the rat-growth test agreed well. Synthetic vitamin B_1 (Merck's vitamin "Betabion") gave results almost identical with those for the natural product. E. B. D.

Toxicological and Forensic

Some Forensic Aspects of Dermatitis. H. E. Cox. (*Medico-Legal Review*, 1937, 5, 123–133.)—Study is made of the record of about 5000 cases of dermatitis, arising from furs or textiles, the results being considered in relation to idiosyncrasy and "reasonably fit" as mentioned in the Sale of Goods Act. Sensitisation by means of organic compounds is discussed in relation to cosmetics, hair-dyes and perfumes. The incidence of dermatitis due to dyed furs is about 1 in 10,000, and to dyed textile fabrics about 1 in a million. (See also *Chem. and Ind.*, 1937, 56, 568.)

Bacteriological

Gastro-enteritis associated with *Proteus vulgaris*. J. D. A. Gray. (*Brit. Med. J.*, May, 1937, 916–917.)—An outbreak of food poisoning affecting at least 18 persons occurred in Avonmouth. All had eaten cockles sold by an itinerant vendor, and only one person who had eaten any of the cockles escaped illness. The incubation period was 3 to 6 hours. Only two of those affected were seriously ill; these took 7 to 10 days to recover, whilst the rest had practically recovered within 24 to 48 hours. The cockles were prepared under very unhygienic conditions; during part of the process of preparation they were kept in salt and water in a galvanised iron bath, which was also used for the family ablutions. Unfortunately, none of the suspected batch of cockles and no vomits were available for bacteriological examination; faeces, however, were examined, and no enteric, dysentery or food-poisoning bacilli were found, but two cases (2 and 3) showed *Proteus vulgaris*. The blood of cases 2 and 3 did not agglutinate any of the Salmonella or dysentery bacilli, but agglutinated several strains of *Proteus vulgaris* to a titre, the one up to, and the other considerably over, the normal limit recognised for the Weil Felix reaction in the diagnosis of typhus fever, and strains isolated from cases 2 and 3 to a titre of over 1–125. The same titre of agglutination was also shown by a strain of this bacillus that was isolated from the rinsings of the bath. It is suggested that this evidence is sufficient to assign the cause of the outbreak to *Proteus vulgaris* Cases of food poisoning proved to be due to *Proteus vulgaris* are rare. D. R. W.

Rapid Detection of *B. tuberculosis* in Milk. M. L. C. Maitland. (*Lancet*, May 29, 1937, 1297.)—Reference is made to the observation of Torrence (1927), followed up by Matthews (1931), Davies (1933) and Cowan and Maddocks (1935), that tubercle bacilli in milk are usually associated with a particular kind of cell, the endothelial cell, which generally occurs in characteristic groups, and that tubercle bacilli are found more quickly, more easily and more efficiently by the examination of films for these cell groups with the 2/3 in. objective and subsequently for tubercle bacilli within such groups. The best conditions for the examination of milk on these lines were studied experimentally, the technique finally adopted is described, and the results thus obtained with the milk of some 950 cows by this technique are recorded. The author found that it was advantageous (1) to centrifuge the milk at a fairly high speed, 2500 r.p.m., for three minutes only; (2) to make films from the surface of the deposit by removal with a loop bent at right angles to the wire; (3) to spread the film of deposit with a slide and not with a loop, the cell groups tending thereby to accumulate round the edges of the film; (4) to wash the films with ether-alcohol before staining; and (5) to examine samples from each udder of the cow separately. It is claimed that as many as 40 films can be examined microscopically in one hour (presumably by one person).

The milk of all the cows of 36 farms, the bulk milk of which had previously been shown to contain tubercle bacilli by guinea-pig inoculation, was examined by this method. The results were as follows:—(*a*) In 11 farms, no tubercle bacilli were found in any sample (confirmed by guinea-pig inoculation in 6 farms); there was a history of the disposal of one or more cows since the original sample was taken. (*b*) In 2 farms, cell groups were found, but no tubercle bacilli (tubercle bacilli were found in a second sample from 1 cow). (*c*) In 21 farms, 1 cow, and in 2 farms, 2 cows, gave milk showing tubercle bacilli (confirmed biologically).

In a second series, the milk of all the cows of 26 farms not previously tested was examined. Two farms each showed 2 cows with tubercle bacilli in their milk (confirmed biologically), and the milk of the remainder of the cows of these 2 farms showed no tubercle bacilli biologically. Bulk samples of milk from 16 of the remaining farms showed no tubercle bacilli biologically; the remaining 8 farms were not checked biologically. D. R. W.

Organic

Detection of the -SH Group by means of Organometallic Compounds. H. Gilman and J. F. Nelson. (*J. Amer. Chem. Soc.*, 1937, 59, 935–937.)—Bismuth triethyl and lead tetraethyl can be used for the detection of the –SH group. They do not react with the hydrogen in –NH and –C ≡ CH groups nor with simple –OH groups (although some strong carboxylic acids undergo generally limited reactions), and there is no interference by azo or nitro groups. Bismuth triethyl was prepared as follows:—To magnesium ethyl bromide solution prepared from 1·4 moles of ethyl bromide in 400 ml. of ether, 200 g. of an ethereal solution containing 0·4 mole of bismuth chloride were added in an atmosphere of nitrogen. (Bismuth triethyl is inflammable in air.) After heating until the reaction was complete, most of the ether was removed on the water-bath by fractionation through an efficient column. The remaining ether and bismuth triethyl were distilled at 4 mm. pressure from an oil-bath, which was heated gradually to a final temperature of 170° C. This distillate was collected in a modified Claisen flask (250 ml.), which was cooled by a mixture of ether and solid carbon dioxide. After distillation of the ether from the distillate, the bismuth triethyl was collected at about 123° C. (150 mm. pressure). *Method of Analysis.*—The usual Zerewitinoff apparatus and method were used, all the work being carried out in an atmosphere of nitrogen. Five ml. of a 25 per cent. (by volume) solution of bismuth triethyl in *n*-butyl ether were run into the side-bulb through a bent pipette with a stopcock. The main bulb, full of nitrogen, was attached to the gas burette, immersed for a few minutes in the water-bath at 25° C., and the system was closed to the atmosphere. The bulb was heated for a definite time on a boiling water-bath, cooled quickly, and then placed again in the water-bath at 25°C. Temperature, volume and pressure readings were made 15 minutes after heating was discontinued. Results (after deduction of blank tests) for numerous compounds, with results for similar experiments with purified lead tetraethyl, are tabulated for various times. They are given as fractions of the reactive hydrogen which reacted in these times. Except for its inflammability, bismuth triethyl is preferable to lead tetraethyl. The latter is highly toxic; bismuth triethyl gives high values for –SH groups and is less interfered with by –OH groups. It is suggested that these organo-metallic compounds may be useful in establishing the existence of thioenolisation in compounds such as thioacetic acid. E. B. D.

Polarimetric Determination of Water in Acetic Acid. G. Toennies and M. Elliott. (*J. Amer. Chem. Soc.*, 1937, 59, 902–906.)—The amount of water in acetic acid can be determined polarimetrically by allowing it to react with a known amount of acetic anhydride in the presence of a small amount of perchloric acid and determining the excess of anhydride by the decrease in optical rotation caused by its reaction with *d*-camphoric acid to form *d*-camphoric anhydride. The perchloric acid acts as a powerful catalyst for both reactions. *Method.*—About 0·0065 g.-mol. of *d*-camphoric acid is weighed in a 25-ml. graduated flask, a definite amount of standardised acetic anhydride is added, and the flask is made up to the mark with the solution to be tested, in which a small amount of perchloric acid of known water-content is dissolved. The amount of acetic anhydride should be such that after reaction with the expected amount of water 3·25 m.ml. of acetic anhydride remains for reaction with the camphoric acid. The amount of perchloric acid present is 0·000125 g.-mol. The amount of acetic acid used is determined by weighing. Polarimetric readings of the solution are taken in a 2-dm. tube until the optical rotation becomes stationary. The specific rotation of the *d*-camphoric acid used is determined in 0·25 *M* solution in glacial acetic acid; that of the anhydride is $[\alpha]_{Hg}$—0·8° (wave length 546·1$m\mu$). The probable experimental error is calculated, and the method is considered accurate to at least ±1 per cent. for water concentrations of 0·1 to 1 per cent. Determinations of 0·1 and 0·6 per cent. of water were made within limits of ±0·001 and ±0·008 per cent., respectively.

E. B. D.

Acidimetric Determination of Glycerol and Erythritol by means of Periodates. M. L. Malaprade. (*Bull. Soc. Chim.*, 1937, 4, 906–910.)—In the author's original method (*Bull. Soc. Chim.*, 1934, 1, 850), which consisted in oxidising glycerol to formic acid and formaldehyde with sodium periodate, followed by titration of the acid in the presence of methyl red, a preliminary approximate determination had to be effected, and the final determination was made in the presence of only a very small excess of sodium periodate, which is slightly acid to methyl red. This method has now been modified by the addition, before the titration, of conc. potassium nitrate solution, which precipitates the periodate as the sparingly soluble potassium periodate. The method can be still further improved by using solid potassium periodate as the oxidising agent. The procedures are as follows:

(A) *With sodium periodate.*—The liquid containing the glycerol is rendered neutral to methyl red by the addition of strong alkali or acid (hydrochloric acid, which reduces periodic acid, must not be used). An excess of a sodium periodate solution is added, and the mixture is allowed to stand for 20 minutes and then treated with conc. potassium nitrate solution; the precipitation of potassium periodate indicates the presence of an excess of periodate. The acid is then titrated with alkali hydroxide solution until the indicator becomes straw-yellow. The quantity of glycerol is calculated from the relation

$$1\ C_3H_8O_3 \rightarrow 1\ HCOOH \rightarrow 1\ NaOH.$$

(B) *With potassium periodate.*—An excess of solid potassium periodate is added to the neutralised solution containing the glycerol, the mixture is shaken for 20 minutes, and the formic acid is titrated as described above. The method is valid in the presence of salts of strong acids and alkalis which do not reduce or precipitate periodic acid, of substances (such as ethyl alcohol) which do not react with periodic acid in the cold, and of substances (such as glycol) which react with periodic acid without the production of acids. Very weak bases and acids weaker than formic acid must not be present. The experimental results quoted show that the method is accurate. It can also be applied to erythritol, 1 g.-mol. of which gives 2 g.-mol. of formic acid. E. M. P.

Depot Fat of the Ceylon Lizard (*Varanus Salvator*, Laur.). T. P. Hilditch and H. Paul. (*Biochem. J.*, **1937**, **31**, 227–228.)—The abdominal fat of a very young kabaragoya or Ceylon lizard (*Varanus salvator*) has been examined. This carnivorous animal enters water readily and feeds on fish, snakes, birds, eggs, carrion, etc. The golden-yellow fat was almost completely liquid at 20° C., and had saponification equivalent 283·9, iodine value 70·8, acid value 4·5, and unsaponifiable matter 1·6 per cent. The fatty acids (54·6 g.) from the hydrolysed fat were separated by the lead salt and alcohol method. The "solid" and "liquid" acids were separately converted into the methyl esters and fractionally distilled in a vacuum. Expressed as per cent. on the total component acids, the acids consisted of myristic, 4·2; palmitic, 29·3; stearic, 9·8; C_{16} unsaturated, 12·3 (mean unsaturation —2·0H); C_{18} unsaturated, 39·6 (mean unsaturation —2·7H); C_{20} unsaturated 4·8 (mean unsaturation —5·5H). The characteristics of lizard fatty acids, as intermediate between those of land and aquatic animals, is confirmed. The presence of 12 per cent. of palmitoleic acid and of small amounts of C_{20} unsaturated acids shows the resemblance to the "aquatic" type of fat, whilst a high content of saturated acids is what is found in the fat of land animals. D. G. H.

Seed Wax of *Simmondsia Californica*. T. G. Green, T. P. Hilditch and W. J. Stainsby. (*J. Chem. Soc.*, 1936, 1750–1755.)—*Simmondsia californica*, Nutt., N.O. *Buxaceae*, is an evergreen shrub indigenous to southern California and southern Arizona, and the nature of the liquid oil obtained from the seeds has already been found to be exceptional (Greene and Foster, *Bot. Gazette*, **1933**, **94**, 826). Four hundred g. of mature seeds were used for the present investigation, and 48 per cent. of a golden-yellow oil were obtained on extraction with petroleum spirit. This yielded approximately equal weights of fatty acids and fatty alcohols. Glycerol was absent. The mixed acids were recovered from the insoluble and soluble lead salts, converted into the methyl esters and fractionally distilled in a vacuum. From the fractionation data obtained it was evident that the acids yielding insoluble lead salts were not saturated fatty acids, but differed little from the main bulk of those acids whose lead salts had remained in solution in the alcohol, and that the acids from the soluble lead salts were for the most part similar to the former, except that not more than 6 to 7 per cent. of the total acids had methyl esters of a mean equivalent of 292·0 and iodine value 71·3, indicating the probable presence of oleic and palmitic acids. The main component acid was found to be an eicosenoic acid, identified as $\Delta^{11:12}$-eicosenoic acid. Small quantities of a higher acid, possibly docosenoic, were also present.

The alcohols were separated by fractional distillation in a vacuum into three main fractions, none of which appeared to be wholly composed of an individual compound. A portion of the second fraction was hydrogenated, and some of the saturated alcohols were recrystallised. Another portion of the hydrogenated alcohols was oxidised with chromic acid in acetic acid solution. A portion of the third fraction was oxidised with permanganate in acetone. Definite evidence of the presence of $\Delta^{13:14}$-docosenol was obtained, and eicosenol (probably $\Delta^{11:12}$-eicosenol) is considered to be the other main alcohol component. So far as is known, no other fatty material from seed endosperm or embryo possesses a similar composition. It may be noted that the seed of *Simmondsia californica* itself has certain morphological abnormalities. D. G. H.

Iodine Value of Derivatives of Cinnamic Acid. A. Lespagnol and J. Bruneel. (*J. Pharm. Chim.*, 1937, **25**, 454–457.)—The (Hübl) iodine values found and calculated, respectively, were as follows:—cinnamic acid (recrystallised several times), 27·7 to 29·4, 171; commercial ethyl cinnamate dissolved in chloroform, 24·8 and 25·0, 144; benzyl cinnamate (recrystallised), 4·5 to 6·7, 106; cinnamyl cinnamate (m.p. 41·5° C.), 83·8 to 87·0, 184; cinnamyl alcohol (recrystallised), 182 and 187, 191. The periods of contact varied from 2 to 12 hours. Care is therefore necessary in interpreting the iodine value of drugs containing cinnamic acid or its derivatives (*cf.* Beaugeard, *Bull. Sci. Pharmacol.*, 1934, **41**, 210), and the method of Vohlmar and Samdahl (*Bull. Soc. Chim.*, 1935, **2**, 826), which is based on the fixation of bromine atoms by double linkages, is therefore preferred. J. G.

Use of Coloured Powders for the Detection of Poison Gases used in Warfare. H. L. Ligtenberg. (*Chem. Weekblad*, 1937, **34**, 321.)—J. Thomann (see *Protar*, March, 1937, p. 81) and A. P. J. Hoogeveen (*Chemie en Luchtbescherming*, 1937) have suggested the use of a powder containing Sudan red for dusting over areas suspected of contamination by mustard gas. A blood-red colour indicates a positive reaction, and this method is preferable to the use of paper impregnated with the reagent, because contact between the gas and the dye is facilitated physically, and because the contrast in colours before and after reaction is more marked (*cf.* Ligtenberg, ANALYST, 1937, **62**, 326). The method, however, is not specific (*cf.* Ligtenberg, *loc. cit.*), and the following modification is recommended:—One part of Sudan red is ground well with 1000 parts of ground chalk, and this powder is then mixed with 3000 parts of non-purified sea-sand. The sand is not essential, but it enables the dye to be distributed more easily and over a larger area. If a positive reaction results, another powder containing 1 part of ferric chloride and 7 parts of ground chalk is dusted over the first, when a green colour is obtained within 1 minute if mustard gas or brom-benzyl cyanide or phenylcarbylamine chloride (which are used to mask it) is present. Carbon dioxide, fatty oils, chloropicrin and diphosgene produce a rust-coloured stain, which may turn green after a prolonged period; benzene and lubricating oils, which may occur on the roads in large cities, do not react. The ferric chloride powder is hygroscopic and should be stored in a suitable container, and it should be used on surfaces (*e.g.* paving stones) which are not too porous, as a dry porous stone can prolong the period of reaction by 30 minutes. J. G.

Inorganic

Method of Qualitative Analysis without the use of Hydrogen Sulphide. M. B. Rane and K. Kondaiah. (*J. Indian Chem. Soc.*, 1937, 14, 46–50.)—The scheme is based on the separation of the basic constituents into five groups. The mixture is dissolved as far as possible in hydrochloric acid, the liquid is boiled with an excess of nitric acid, and evaporated to dryness, and the residue is digested with nitric acid. The insoluble portion may contain silver, antimony, tin and any insoluble matter (Group I). To the solution, after filtration, is added ammonium sulphate solution, and the liquid is boiled; the precipitate, which is filtered off, may contain barium, strontium, calcium and lead (Group II). A portion of the filtrate is tested for phosphate by means of ammonium molybdate; the rest of the solution is heated, and a liberal excess of ammonia is added, followed by ammonium phosphate until no further precipitation occurs; the precipitate may contain hydroxides, phosphates or arsenates of iron, aluminium, chromium, bismuth, manganese, calcium and magnesium (Group III). The liquid, after filtration, is boiled with an excess of sodium hydroxide, giving a precipitate which may contain cobalt, nickel, copper, cadmium and mercury (Group IV). The liquid may contain zinc and arsenic (Group V). The methods suggested for the detection of the constituents of the groups follow customary lines. Alkali metals are tested for in the original mixture after removal of other bases by "barium hydroxide and sulphuric acid treatment." S. G. C.

New Method for the Determination of Cadmium and its Separation from Zinc. C. Mahr and H. Ohle. (*Z. anal. Chem.*, 1937, **109**, 1–5.)—Cadmium solutions containing thiourea, when treated with ammonium tetrathiocyanato-diammine-chromiate (Reinecke's salt), yield a complex precipitate of the composition $[Cd(CSN_2H_4)_2][Cr(CNS)_4(NH_3)_2]_2$, containing 12·47 per cent. of cadmium. The dried precipitate may be weighed, or its chromium-content determined volumetrically after conversion into chromate. A single precipitation separates cadmium from arsenic, antimony, nickel, cobalt, iron, manganese, chromium, aluminium, alkaline earths and alkalis, as well as from 1000 parts of zinc. The acidity of the cadmium solution should be *N* (or less if other metals preponderate), and its thiourea-content 1 per cent.; it is treated with a filtered solution of Reinecke's salt, containing 1 per cent. of thiourea, in moderate excess. After ½ to 1 hour's cooling in ice-water with occasional agitation, the liquid is filtered through a porous glass-crucible, and the pale-red, finely-crystalline precipitate is washed with ice-cold 1 per cent. thiourea solution, which is finally displaced by 3 to 4 washes with ice-cold absolute alcohol. The precipitate is dried at 110° to 120° C., and weighed.

For the volumetric determination of cadmium, the precipitate is collected on a filter-paper, washed with 1 per cent. thiourea solution, and gently ignited (with the filter-paper) in a nickel crucible. The residue is fused with sodium peroxide, the mass is dissolved in water, and the solution is boiled for 15 minutes for the destruction of hydrogen peroxide. The chromate is titrated in the acidified liquor with iodide and thiosulphate in the usual manner. W. R. S.

9-Methyl-2-3-7-trioxy-6-fluorone as Reagent for the Detection of Antimony. R. Duckert. (*Helv. chim. Acta,* 1937, **20**, 362–367.)—The reagent is used in saturated alcoholic solution acidified with hydrochloric or sulphuric acid. It yields a red precipitate with antimony in acid tartrate solution, preferably at *p*H 4. The reaction is stated to be highly sensitive and to be given equally well by ter- and quinquevalent antimony. Some other ions, in particular, cerium and germanium, give similar colours; iron gives a dark-violet colour. The test is being investigated, and further details are to be published shortly. A method of preparing the reagent is outlined. S. G. C.

Atomic Weights of some Radiogenic Leads. G. P. Baxter, J. H. Faull, Jr., and F. D. Tuemmler. (*J. Amer. Chem. Soc.*, 1937, **59**, 702–705.)—The following results have been obtained in the determination of the atomic weights of certain radiogenic leads:

Cerussite, Wallace, Idaho, U.S.A. (Common)	207·21
Samarskite, Glastonbury, Conn., U.S.A.	206·34
Pitchblende, Beaverlodge Lake, N.W.T., Canada	206·08
Pitchblende, Katanga, Africa	
Black, insoluble portion	206·04
Yellow, hydrochloric-acid-soluble portion	206·05

It is pointed out that these values, together with the percentages of important components, point to the presence of several per cent. of common lead in all three radioactive minerals.

Colorimetric Determination of Ferric Iron with 7-Iodo-8-hydroxyquinoline-5-sulphonic Acid. J. H. Yoe and R. T. Hall. (*J. Amer. Chem. Soc.*, 1937, **59**, 872–879.)—The properties of 7-iodo-8-hydroxyquinoline-5-sulphonic acid (known as "ferron"), which was suggested by Yoe (*J. Amer. Chem. Soc.*, 1932, **54**, 4139; Abst. ANALYST, 1933, **58**, 54) as a reagent for the colorimetric determination of ferric iron, are examined in detail. The solubility of ferron in various solvents, its physical and chemical properties, the nature of the colour with ferric iron, the influence of various ions, sensitivity, conformity to the Lambert–Beer law, and the effects of *p*H, of ageing, and of temperature were investigated. The maximum solubility (0·7200 g./100 ml. of solution) was obtained in a water-acetone (1:1 by vol.) mixture. From the results the following are considered to be the optimum experimental conditions:—Sufficient reagent should be added to give 3 mols. of ferron per atom of ferric iron. For Nessler-tube work, using 50-ml. (tall form) tubes, a fixed amount of reagent is added over a whole range of iron concentration. For iron concentrations of less than 1 p.p.m., a solution free from any interfering ions is prepared, the acidity is adjusted to *p*H 2·5 by means of hydrochloric acid and potassium phthalate buffer, and 0·25 ml. of the ferron reagent is added. The colour develops at once. The solution is diluted to the mark and mixed thoroughly. For iron concentrations of 1·0 to 2·0 and above 2·0 p.p.m., 1 ml. and 2 ml. respectively of reagent are added; concentrations greater than 4·0 p.p.m. should not be used. The maximum sensitivity is from 1 to 2 p.p.m. of ferric iron. The sample solution must always be tested with Congo red or methyl orange paper and, if necessary, the *p*H must be approximately adjusted before the buffer is added.

Iron has been determined in glass sand and glass, in rocks, and in alloys by this method, the weight taken being one which gives 1 to 2 p.p.m. of iron. (A rough preliminary analysis is made if necessary.) In glass sand and glass the iron is determined as follows:—A sample is weighed after drying at 110° C. It is fused with sodium carbonate in a platinum crucible, cooled, and treated by the perchloric acid method (Hillebrand and Lundell, *Applied Inorganic Analysis*) for the dehydration of silicic acid. The silica is filtered and washed with dilute hydrochloric acid and then with water. To the filtrate in a porcelain dish, ammonium hydroxide is added until Congo red paper just shows acidity. After sufficient evaporation on a steam bath, the iron is determined colorimetrically as described above, 10 ml. of the buffer solution being used. If too much aluminium is present, it must be removed before the determination of the iron (or, a corresponding amount of aluminium salt may be added to the standard). Cupric ions interfere with this test when only 0·2 p.p.m. are present. Stannous, stannic, and titanium ions and dichromate and nitrite ions must not be present in concentrations of more than a few tenths of a part per million. For precise work they should be removed entirely. Fluoride must be removed, because it causes partial bleaching, and relatively large amounts of phosphate retard, but do not prevent, the reaction. Cobalt, nickel, and chromium should be present only in limited amount; aluminium ion may be present up to a concentration 5 times that of the ferric ion. Over the range of concentrations examined, the colour follows the Lambert–Beer law. Ageing and temperature (15° to 40° C.) do not affect the colour. (*Cf.* Yoe, *loc. cit.*, and Clark and Sielong, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 256–7; Abst., ANALYST, 1936, **61**, 632.) E. B. D.

Detection of Periodate. R. Fabre and T. Tomesco. (*J. Pharm. Chim.*, 1937, **25**, 241–244.)—A solution of zinc acetate produces a precipitate in an acetic acid solution of periodate, but none in iodate solution under the same conditions. The authors use a reagent containing 2 per cent. of zinc acetate in 3 per cent. acetic acid. The reaction detects 0·001 g. of periodate ion in 1 ml. at room temperature; in hot solutions the sensitiveness is 10 times greater. The composition ascribed to the precipitate agrees with the formula $Zn_5(IO_6)_2$. W. R. S.

Analysis of Refractories. E. Azzarello and F. Abramo. (*International Association for Testing Materials, London Congress, Group B, Paper No.* 59, *May*, 1937.)—A modified procedure is proposed to overcome difficulties in the usual method due to the accumulation of salts in the solution incidental to the successive precipitations of sesquioxides, calcium and magnesium. Silica is first separated and determined as usual. The solution containing the other constituents is divided into two parts. In one part, zirconium, aluminium and titanium are determined by the method of Grewe (*Arch. Eisenhüttenwesen*, 1934, **7**, 505). In the other part, iron, manganese, titanium, zirconium, calcium and magnesium are precipitated together as follows:—The solution is approximately neutralised with sodium carbonate, diluted to 200 ml., and slowly poured while hot, with vigorous shaking, into 25 to 35 ml. of hot sodium hydroxide solution (sp.gr. 1·332). Fifteen ml. of hydrogen peroxide (3 per cent.) are added, the solution is boiled for 10 minutes, 1 g. of sodium carbonate is added, and the liquid is diluted to 300 ml. with boiling water, kept hot for 2 to 3 hours, and then left for 16 to 18 hours. The precipitate is filtered off on a sintered glass filter and washed with 1 per cent. sodium carbonate solution, the filtrate is rejected, and the precipitate is dissolved in hydrochloric acid. The solution is diluted to 100 to 150 ml., and the iron, etc., is precipitated with ammonia and hydrogen peroxide, re-precipitation being advisable if the precipitate is voluminous; the combined filtrates are reserved. The precipitate is dissolved in dilute sulphuric acid, and the solution is divided into two portions. To one portion (diluted to 100 ml.), 2·5 g. of ferrous sulphate are added, and then hot sodium bicarbonate solution (8 per cent.) until a persistent turbidity is produced; a further 4 ml. of the bicarbonate solution are added, and the liquid is boiled for 1 minute and then filtered with the aid of suction. The precipitate, which contains the zirconium and titanium, and in which these elements may be determined if desired, is washed with hot water. The turbid filtrate, acidified with sulphuric acid, is concentrated by evaporation, and manganese is determined by the bismuthate method. In the second portion of the solution, iron is determined by any convenient method. The reserved ammoniacal filtrate, mentioned above (100 ml.), to which has been added 2·5 g. of ammonium acetate, is heated to boiling, and the magnesium is precipitated by the addition of a moderate excess of 5 per cent. alcoholic solution of 8-hydroxyquinoline. After standing for half-an-hour the precipitate is filtered off on a sintered glass filter and washed with a hot dilute ammoniacal solution of ammonium acetate, followed by alcohol containing 0·7 per cent. of ammonia (sp.gr. 0·9); the magnesium is determined gravimetrically or volumetrically as usual with this precipitate. The filtrate is evaporated to 100 ml., and calcium is precipitated as oxalate from the boiling liquid by the addition of 20 ml. of a boiling solution of ammonium oxalate; calcium is determined as usual. Alkali metals are determined separately in the refractory by the Lawrence Smith method. S. G. C.

Microchemical

Volumetric Determination of Small Amounts of Water by means of Cinnamoyl Chloride. C. J. van Nieuwenburg. (*Mikrochemica Acta*, 1937, 1, 71–74.)—On investigating a number of acid halides for use as substitutes for naphthyloxychlorophosphine in the determination of less than 5 mg. of water, cinnamoyl chloride was found to be most satisfactory; it is much less expensive, and does not show the irregularities often encountered with the phosphine. It reacts readily with water, and is practically non-volatile by itself. When used with a spiral absorption tube of 7 mm. internal diameter it gave results concordant within 0·1 mg. The results were 0·02 to 0·09 mg. too high, which the authors attribute to incomplete drying of the air and to the quartz tube used. These points are being further investigated. J. W. M.

Micro-determination of Glycerol in Fats and Phosphatides. G. Blix. (*Mikrochemica Acta*, 1937, 1, 75–77.)—The method is based on a methoxyl determination according to Vieböck and Brecher (*Ber.*, 1930, 63, 3207, and Friedrich, *Die Praxis der quantitativen organischen Mikroanalyse*, Leipzig, 1933). The apparatus is modified from the Pregl methoxyl apparatus. The distilling portion is attached by a ground-glass joint to the distilling tube, and the washing device has a glass tap underneath for emptying, instead of a cork; there is also a ground-glass stopper to close a side-tube on the washing device for cleaning purposes. The delivery tube is also closed above by a ground-glass stopper. The lipid material is dissolved in pure benzene, and a definite volume (0·3 to 3 ml.) is pipetted into the distillation flask. The benzene is removed by gentle evaporation in a slight current of air, in the presence of 2 ml. of hydriodic acid (sp.gr. = 1·70) and a few pieces of red phosphorus. The washing device is charged with 0·3 ml. of 5 per cent. sodium thiosulphate solution, and the receiver with 3 ml. of 10 per cent. sodium acetate in glacial acetic acid, and 2 to 3 drops of bromine. A stream of purified nitrogen is passed through slowly at such a rate that there is always one bubble in the receiver, and the distillation flask is heated for 3½ hours in a glycerin bath at 120° to 125° C. The lipids are hydrolysed and the isopropyl iodide formed from the glycerol is collected in the receiver, the contents of which are titrated according to the method of Vieböck and Brecher. Extremely good results are recorded. J. W. M.

Micro-detection of Nitrate. F. Werr. (*Z. anal. Chem.*, 1937, **109**, 81–91.)—The method is based upon the ready nitration of xylenol ($CH_3 : CH_3 : OH = 1 : 3 : 4$) by nitrates in presence of sulphuric acid, the volatility of nitroxylenol, and its property of forming a coloured alkali salt. The procedure is almost as simple as the baryta-water test for carbon dioxide. The reagents required are sulphuric acid (75 per cent. by vol), 0·5 *N* sodium hydroxide solution, and xylenol (A.R.). The apparatus consists of a 150-ml. flask fitted with a perforated rubber stopper carrying a doubly-bent glass tube, the vertically-descending member of which is water-cooled and dips into 2 ml. of 0·5 *N* sodium hydroxide contained in a test-tube.

The material (0·1 g. of solid, or a solution containing this amount of dissolved substance) is treated with sufficient distilled water to bring the volume to 100 ml., the solution being filtered if necessary. Preliminary tests should be made for hydrogen peroxide or per-acids; if present, they are destroyed by boiling the alkaline solution. One ml. of the prepared solution is introduced into the flask containing 5 ml. of 75 per cent. sulphuric acid and one drop of xylenol, and the flask is closed with a stopper and left in the cold for 10 to 15 minutes, with occasional shaking. Water (20 ml.) and a few glass beads are added, and the stopper with outlet-tube inserted. The distillation is conducted so as to yield about 10 ml. of distillate in 5 minutes. After cooling, the alkaline liquid in the test-tube is viewed against a white background; a barely perceptible yellow colour reveals 0·001 mg. or less of nitrogen as nitrate. The depth of colour increases with the nitrate-content, large amounts giving a reddish-yellow to red colour. A blank test should be made with the reagents, and the apparatus should be flushed with steam before and after use. Nitrites give a positive reaction and should be destroyed before the test is made. The sensitiveness is 0·001 mg. of nitrogen at a concentration of 1:1,000,000. The method is considered specific and more sensitive than the usual reactions, while it is not so hypersensitive as the diphenylamine test.

When, as described above, the test is carried out on 1 mg. of the sample, the presence of even a high proportion of chlorides and of most other salts, in the sample, has no considerable effect; but if a larger quantity, *e.g.* 100 mg., were used, a high proportion of sulphides, halides, oxyhalides, dichromates, etc., might cause serious errors. W. R. S.

Micro-determination of Iodine by a Catalytic Method. E. B. Sandell and I. M. Kolthoff. (*Microchemica Acta*, **1937, 1,** 9–25.)—A procedure is described for the determination of quantities of iodide of the order of 0·05 to 3γ in 1 ml. of solution or in a suitable amount of solid sample (sodium chloride). The method is based upon the strong catalytic effect of iodide on the reaction between ceric sulphate and an excess of arsenious acid in dilute sulphuric acid (1·5–2 *N*). The effect of the following factors on the velocity of the reaction was studied: the iodine concentration, the temperature, and the presence of foreign substances. The velocity increases with increased iodine concentration up to 1γ per ml., and also increases with rise in temperature (from 4 minutes at 2·5° C. to 1 minute at 25° C.) under the following conditions:—The potassium iodide solution of known concentration is measured from a micro-burette into a 2 × 7 cm. micro-beaker, and is followed by 2 ml. of 0·1 *N* sodium arsenite solution, 1 ml. of 6 *N* sulphuric acid, 0·1 ml. of 0·001 *M* *o*-phenanthroline ferrous sulphate (as indicator), and water to bring the total volume to 4 ml. The mixture is poured quickly into another micro-beaker containing 1·0 ml. of 0·1 *N* ceric ammonium sulphate solution and sufficient sulphuric acid to make the acidity 1·5 *N*. A stop-watch is started at the instant of mixing. The mixed solution is quickly transferred back to the original beaker, immersed in a water-bath at known temperature and shaken gently. The first appearance of a pink tinge is taken as marking the completion of the reaction. The presence of foreign salts leads to a considerable change in reaction velocity. With an unknown solution this difficulty can be overcome by adding a suitable known amount of iodine and comparing the catalytic activity of the solution so obtained with that of the original solution. It is best to make the volumes of both solutions the same for the comparison. In the absence of chloride the linear relationship between catalytic activity and iodine concentration fails for low concentrations. Therefore, if chloride is not present in the sample, it is necessary to add about 10 mg. of sodium chloride. The concentration of iodine in the reaction mixture should generally be less than 1:2,000,000, for amounts of iodine (as iodide) from 0·05 to 1γ; in the presence of 5 to 15 mg. of sodium chloride the mean error is about 10 per cent.
J. W. M.

Summary of Microchemical References in 1936. P. Haas. (*Mikrochemica Acta*, 1937, 1, 106–119.)—Thirteen pages of references are arranged in alphabetical order of the authors under the following subjects: inorganic (preparative and analytical), physical and physical methods, organic (preparative and analytical), biochemistry, medical chemistry, pharmacy, toxicology and forensic chemistry, applied chemistry (technical, mineralogical, agricultural, foodstuffs, etc.), and apparatus. J. W. M.

Physical Methods, Apparatus, etc.

Inflammability of Cork and Wood Dusts. W. Kühn. (*Chem.-Ztg.*, 1937, 61, 406–408.)—Dusts are classified into 3 categories, *viz.* (1) those which both ignite and transmit combustion readily; (2) those which ignite readily, but do not readily transmit combustion; (3) those which are stable in both respects. Cork and wood dusts belong to the first category, and their behaviour is governed by the following factors:—*Sp.gr.*—Average values are: cork, 0·24 and wood (pine and fir) 0·34, so that the former will float more readily. *Particle-size.*—Ignition temperatures for samples of cork dust completely passing a 200-mesh sieve, almost completely passing it, and passing to the extent of 50 per cent. are: 975° C. (flame spreads rapidly), 620° C. (0·6 per cent. unburnt) and 630° C. (flame spreads rapidly), respectively. Corresponding data for samples of wood dust which was too flocculent to be sieved, which could be sieved with difficulty, and which was sieved to the extent of 20 per cent. are: 985° C. (light smoke), 610° C. (3·2 per cent. unburnt), and 635° C., respectively. Unsieved cork developed on ignition an explosion-pressure of 0·52 atm., and sieved wood 0·9 atm. Sieve tests have also shown that the (average ?) size of the particles of cork dust is 7·7 per cent. less than that of wood dust, and that the former dust is more uniform in size. No traces of wood were found in the bronchial secretion 14 hours after exposure to an atmosphere containing wood dust, whilst with cork dust traces were still to be found after 48 hours; the former dust promotes sneezing more readily than the latter, probably on account of the larger size and coarser structure of the wood-dust particles. *Water-content.*—As this increases, the ignition-temperature rises, but smoke-formation is not necessarily affected. The raw materials and air-dry dust may contain the following percentages of water, respectively:—Wood, 15 to 40 (mean 28), 7 to 12 (mean 9); cork, 4 to 18 (mean 8), 2 to 7 (mean 6). In moist air, however, wood dust will absorb five to six times its weight of moisture, and this lowers further its tendency to ignite. *Particle structure.*—This depends on the type of disintegrator used. Particles of wood dust vary considerably in size and shape and may be fibrous, angular or rod-shaped and produce aggregates of these forms. Cork dust particles, however, are usually round plates with serrated edges, and are associated with very small particles, some of which are 0·08μ in diameter. Unlike wood particles, they do not "ball," but are always mobile. *Ease of oxidation.*—This is primarily a function of the size, structure and shape of the particles, since it depends on the surface exposed. The heat generated by the disintegration process is also important, and temperatures of 70° C. for wood and 98° C. for cork may be reached; it has also been stated that pyrophoric carbon may be produced in this process. To summarise, the evidence suggests that cork dust is more liable to ignition than wood dust. J. G.

Examination of Essential Oils by Measurement of the Ultra-violet Absorption. D. Van Os and K. Dykstra. (*J. Pharm. Chim.*, 1937, 25, 437–454.)—Lambert–Beer absorption-curves, obtained by the usual method, are given for the range 200 to 400 $m\mu$. A Scheibl rotating sector-disc was used to control the intensity of the comparison spectrum, and the source of radiation was a spark-discharge passing between two tungsten electrodes. The solvent used was alcohol purified by distillation over iodine, followed by decolorisation by means of zinc and several distillations over freshly-burnt lime. The wave lengths (in $m\mu$) of max. absorption of the various oils and their constituents were as follows:—*Oleum Anisi*, 260 (anethole, 260, min. 237; methyl chavicol, 225·5 to 285, min. 245·5 and 282·5). It was therefore possible to use the method to calculate the amount of anethole present (87 and 89 per cent. in the two samples tested), and also to detect adulterants of oil of anise (which lower the anethole content) and conversely, oil of anise in other oils. *Oleum aurantii*, 320 (residue after distillation 319, min. 274). The presence of methyl anthranilate is not apparent from the absorption curves, and *d*-limonene and *n*-decyl aldehyde have little influence on them; if ethyl phthalate is present the shape of the curve is altered considerably. *Oleum Bergamottae*, 311, min. 278. These values (and another min. at 238) were also obtained from the residue after distillation. The effects of linalyl acetate, linalol, limonene (*cf.* supra) and nerol are of less importance. All adulterants modify the shape of the curve, especially if they are aromatic in character. *Oleum Cajuputi* gives curves with no characteristic features. Cineole is very transparent to ultra-violet light, and *d*-terpineol gave a max. at 231$m\mu$. *Oleum Cari* showed the features of *d*-carvone rather than of *d*-limonene (*cf. supra*), namely, max. at 318 and 225, and min. at 282$m\mu$. Adulteration with aromatic ethers produces other maxima, whilst adulteration involving removal of carvone decreases the absorption. *Oleum Caryophylli* gave curves having the characteristics of eugenol, the proportion of which (86 and 89 per cent.) may therefore be calculated; they had max. at 282 and 229, and min. at 253. Acet-eugenol had a max. at 272, whilst caryophyllene absorbed continuously. Most adulterants decrease the absorption. *Oleum Chenopodii.*—Max. at 273, 264 and 258, and a min. at 235, were attributed to cymene, ascaridole being without effect, as shown by its continuous absorption curve. Adulterants (*e.g.* mixtures of anethole, cineole and menthol and ethyl benzoate and salicylate) modify the curve considerably.

J. G.

Reviews

THE BIOCHEMISTRY OF THE LIPIDS. By H. R. BULL, Ph.D. Pp. ix + 169. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1937. Price 13s. 6d. net.

This is a textbook intended for graduate students, and the author has endeavoured to give an account of the present knowledge of the biochemistry of fats in less than 160 pages. He is to be congratulated on having gone a very long way towards success; he has written an "up-to-date, readable" book, which covers the ground and keeps, on the whole, due perspective which adopts the fresh points of view developed in this field in recent years, and breaks away from the older, stereotyped treatment of the subject that has persisted too long in most textbooks on the subject.

If the reviewer could only leave it at that, it would be well. But Dr. Bull has gone so far in showing how a comparatively short book of this scope can be written as to cause regret that it has not been done still better. The chief criticism one would offer is that, in so brief a volume, every page is valuable, and that the matter in not a few pages might have been omitted, or at least drastically curtailed. A few instances in support of this contention are: The sulphated and sulphonated detergents (pp. 7 and 8) have no connection with biochemistry, unless it be to point the analogy between their surface and interfacial properties and those of the natural phosphatides (an analogy to which no reference is made); moreover, there are at least two mis-statements in this section. The table on p. 9, the structural formulae on p. 20 and p. 34, and in some other places, and a number of other bulky tables of physical data not wholly necessary for the purpose of the book might have been omitted or abbreviated, and space thereby set free for fuller treatment of other topics.

The plan of the book is good, but some of the chapters are disproportioned; that on "fats and oils" might well have been expanded, perhaps at the expense of those on "sterols" and on "alcohols, waxes and hydrocarbons." It is impossible to deal adequately with sterol and related chemistry in the course of the book under review, and it would have been better to abandon the attempt to do so. Waxes and hydrocarbons, on the other hand, seem to get more space than their bearing on the main theme warrants. The chapters on "phospholipids" and emulsions are excellent, compact, and modern, and it is by comparison with these that the rest of the book appears capable of improvement. The book is marred somewhat by minor errors; *e.g.* clupanodonic acid is given as $C_{18}H_{28}O_2$ (p. 5), whilst references to authors quoted in the text are given or omitted somewhat haphazardly and the literature references, where given, are sometimes incomplete.

Discussion of current hypotheses is, of course, a matter in which each is largely entitled to his own opinion. Thus, while Dr. Bull (p. 11) says that any theory of the formation *in vivo* of fatty acids must account for the occurrence of only even numbers of carbon atoms in the molecule and for the general absence of short-chain acids, the reviewer feels that such a theory must, even more, explain the overwhelming abundance in nature of oleic acid, with the ethenoid bond dividing the carbon chain into two groups containing 9 carbon atoms; and where (p. 152) he says that it "appears as if the mechanism for fat synthesis had partly failed" in the case of milk-fats, the writer would suggest that the mechanism in question is probably more, instead of less, elaborate than usual. Again, in the course of an exceedingly fair and full survey of the reviewer's recent contributions in this field, Dr. Bull seems (p. 92, par. 2) to miss the point of the oleic-stearic glyceride relationships which have been established in ox, sheep and pig depôt fats. On pp. 95–97, in discussing changes in fats during seed ripening, a reference should certainly have been made to the important work of Ivanov and of Eyre on linseed.

The book is prefaced by an account of the various formal classifications of fats or "lipids" which have been proposed from time to time. It appears uncertain how far such arbitrary classifications serve any useful purpose beyond that of presenting to the student a simplified or bird's-eye view of the field under discussion. Even so, the classification of the unit-substances—the fatty acids, alcohols, etc.—by Bloor as "derived lipids" seems singularly incongruous. Do architects or builders classify bricks and mortar as "derived houses"?

T. P. Hilditch

SOIL CONDITIONS AND PLANT GROWTH. By Sir E. JOHN RUSSELL. 7th Ed. Pp. viii + 655. London: Longmans, Green & Co., Ltd. Price 21s. net.

A scientific work which has reached a seventh edition in 27 years must be considered as a "best seller." The success of this volume is due not only to the importance of the subject, but also in a large measure to the readable manner in which the facts relating to soil problems are presented. The author has the advantage of a long experience at an institution which, for nearly a century, has been known as a centre of soil research.

The soil in relation to the earth itself is but as a thin film of tarnish and altered slag on a sphere of iron alloy, its thickness being less than a millionth of the radius of the globe, and its mass less than a ten millionth of the earth's mass. Yet on this thin film, with its gaseous envelope, the whole life of the earth depends. Prof. V. M. Goldschmidt, in a lecture recently given to the Chemical Society, has endeavoured to show why the distribution of elements on the earth's crust is so different from what, on considerations of density, it must be in the interior and is mainly silicious rather than ferruginous. Sir John Russell devotes his six hundred odd pages to a discussion of the thin disintegrated upper layer of the crust, which has become what we know as soil, and its relation to the growing plant.

The practical study of the soil and the plant has occupied mankind from prehistoric times, and a mass of empirical data has been accumulated which scientists have sought to explain and augment. The mere fact of plant growth is amazing; so little is put in the soil, so much taken out, year after year, until the soil shows signs of exhaustion. Whence comes all the substance of the plant? Theodore de Saussure, son of the inventor of the hair hygrometer, first showed that plants both breathed like animals and, unlike animals, were able to decompose the carbon dioxide of the air and to build up from it the greater part of their substance, whilst the part that entered through the roots was small but essential, supplying nitrogen which was not assimilated direct from the air and ash constituents "qui peuvent contribuer à former, comme dans les animaux, leur parties solides ou osseuses," and that the absorption from the roots was selective. It was some time before this view was generally accepted; in fact, many of those who contributed most to a correct knowledge of the chemistry of the soil showed great acuity of vision in some directions, but a remarkable blindness in others. Progress was hampered by the limitations of the chemistry of the period. It is, however, remarkable to note how new ideas on chemistry and new methods of investigation have been applied to the study of the soil, as well as the great contribution made by sciences other than chemistry to the study of soil problems. Consider on the one hand a mass composed of particles of all sizes, from colloid dimensions to large stones, in all states of aggregation from powder to large clods, made up of complex silicates, quartz, carbonates, with dead organic matter, continually being changed by weathering and the varied activities of a vast mixed population of bacteria, protozoa, fungi, algae, molluscs, insects and worms, the numbers of the various groups of the smaller organisms varying greatly even from hour to hour, the mass having a varying water-content, free, adsorbed and combined, and being under some conditions so hard that it cannot be dug, and at others thixotropic, its properties profoundly modified by changes of *p*H, contributing its offering to the plant in a very dilute solution around and between its particles, and, on the other hand, the plant itself with its delicate system of root hairs. To gain anything like a clear notion of soil conditions and plant growth it becomes obvious that the best endeavours of a group of workers in several sciences, actively collaborating are necessary, and it is not surprising that divergent views are held on many points which on first examination appeared amenable to a simple explanation.

This book gives a good conspectus of the many aspects of the subject in what must be considered a very concise form, with full references to the original sources of information. The reviewer has noticed only one ambiguous or ungrammatical sentence. Referring (on p. 147) to plants as having "synthesised complex organic substances containing much stored up energy," the author says, "After death these substances are added to the soil and so impart the mineral matter stores of energy which *they* (the italics are the reviewer's) had not previously possessed"; and one misprint (p. 269) where a discussion of podzolisation is headed "The Process of Polarization." Even Homer nods!

Of the many contributions made by the author to agricultural science, this authoritative survey of a rapidly growing subject is perhaps one of the most valuable.

J. H. COSTE

CANNING PRACTICE AND CONTROL. By OSMAN JONES, F.I.C., and T. W. JONES, B.Sc. Pp. xii + 266. London: Chapman & Hall, Ltd. 1937. Price 25s. net.

The authors' Preface states that "their aim has been to put together a book of practical value that would include those items of information the canner needs if he is to put on the market a properly processed foodstuff. . . . The definition of canned food that has been adopted is that of foodstuff hermetically sealed and processed in a metal container." It is stated further that "much of purely academic interest, particularly in regard to the chemistry of foodstuffs in general, has been deliberately omitted." The object has been not to compile a treatise, but rather a bench book.

These statements and others in the Preface naturally limit criticism. Since this is the first book on Canning to be published in this country, its announcement was awaited with great interest, and two classes of readers looked forward to receiving it—the expert canner and the young technologist starting his career in a canning factory. The expert will be disappointed at such scanty treatment of the subject where there was room for extended discussion; the beginner will welcome the book for its outline of the main problems involved in canning.

The importance of the laboratory in the food factory is again and again emphasised, and it is very evident that the chemist must have a sufficient knowledge of food bacteriology. Indeed, the bacteriological bias is very marked throughout the work—and rightly so.

Fifteen chapters cover a wide range of topics, from the design and equipment of the cannery and its laboratory (including water supply, cannery waste and hygiene) to the raw materials, the can itself, and the general micro-biology involved. A useful chapter deals with the important subject of food values and vitamins.

There is a chapter on the preparation and use of culture media, another on the staining of specimens for microscopical examination, and one on cultural notes of the principal food-spoiling organisms (excellently illustrated).

The authors enjoin the reader all too frequently to consult the original literature. Thus, corrosion of the container is dismissed in twenty-four lines. It is not modern practice (as stated on p. 30) to stamp out can ends and then in another press to effect corrugations; the whole is effected in one operation. Again, in contradistinction to the statement on p. 40, lids are date coded *before* closing the cans. Although Chapter VI details certain tests for tinplate, no mention is made of the now routine mechanical tests, such as the Erichsen test or the Jenkins bend test, which assume considerable importance in high-speed can-making plants. The gelatin-ferricyanide test for porosity of tinplate is described on p. 90, but not the best method, which is to employ Ferraco paper, this securing a rapid and permanent record of the condition of the tinplate surface.

The experienced analyst will find several points on which to join issue with the authors, who have simply detailed the more elementary routine methods.

The bacteriological treatment is adequate for ordinary routine purposes, and it is here that the book really merits its claim to be a bench book. Of course, special problems involving special bacteriological investigations arise in all food factories. Then long experience or a special training is called for. The reviewer notes with pleasure the authors' outright dismissal of "ptomaine poisoning."

Paper, printing and binding leave nothing to be desired. The illustrations are exceptionally fine. Expansion of the text in the next edition to include adequate treatment of the fundamentals of the chemistry and engineering of canning could make this work the standard in its field. WILLIAM CLAYTON

SOAP: ITS COMPOSITION, MANUFACTURE AND PROPERTIES. By W. H. SIMMONS, B.Sc. 4th Ed. Pp. 140. London: Sir Isaac Pitman & Sons, Ltd. 1936. Price 3s.

The appearance of a new edition of this popular book will be welcomed by the large number of persons who have direct and indirect contact with the industry. For a book of such a modest size a clear picture is given, with most of the branches, including glycerin recovery, well portrayed in their correct proportions; thus, brief details are included of many technical points, and warnings are given to the inexperienced of many of the pitfalls that may be encountered.

The technical information is well related to the commercial description of the products, but it is felt that the section on soap powders has not been brought quite up to date. This revised edition, however, includes references to many advances that have taken place recently in the soap industry, such as those which relate to improvements in manufacture, in the form of the soap products, in medicated soaps and in such associated materials as silicates and phosphates, and makes brief reference, under "soap substitutes," to sulphonated compounds. L. V. COCKS

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

ARTHUR ROBERT LING

WITH the passing of Arthur Robert Ling on May 14th at the age of 75 the chemical profession has lost an enthusiast whose work ever bore evidence of intensive and careful thought and painstaking investigation.

The foundation for his chemical career was well and truly laid under the late Professor H. E. Armstrong at Finsbury Technical College in the early eighties, and his first contact with commercial life was made as junior chemist in the laboratories of the Beetroot Sugar Association of London, where he subsequently became chief chemist. In 1898 he joined forces with the late B. E. R. Newlands, and for five years they practised jointly as sugar specialists and general consultants. Ling then started an independent practice in Great Tower Street, widening his specialist sphere to include brewing and malting.

His natural bent towards research, which was first developed at Finsbury in work on derivatives of quinones, continued throughout his career. His association with sugar, starch and other carbohydrates roused his interest in the then obscure chemistry of these substances, and in the first decade of the present century he published many papers on the action of diastase on starch and the resulting products. His interest in this branch of research never flagged, and, indeed, his last publications were on kindred matters.

Ling became a member of our Society in 1894, served on the Council in 1899–1900, and again in 1908–9, and was a Vice-President in 1911–12. He was Honorary Secretary and subsequently Chairman of the London Section of the Society of Chemical Industry, and served on the Council of the Chemical Society. He was elected a Fellow of the Institute of Chemistry in 1888.

When it was decided to start courses of instruction on the fermentation industries at the Sir John Cass Institute, Ling was appointed lecturer. This was a prelude to his appointment, in 1920, to the Chair of Biochemistry of Fermentation at Birmingham University as the successor of Adrian Brown. Ling was never really at home in commercial circles and he now found his true niche—one that he filled with distinction. His services to the University were officially recognised when the Honorary Degree of M.Sc. was conferred upon him, and again on his retirement in 1931, when he was awarded the title of Emeritus Professor.

For many years he was Technical Editor of the *Brewers' Journal* and he was Editor of the *Journal of the Institute of Brewing* for a quarter of a century.

He had a very wide knowledge of contemporary scientific literature and himself contributed a full quota to it. A great many of his original studies were published jointly with those assisting him in the work, and this was typical of the encouragement that he gave to younger men.

He was generous and cheery in disposition, although he had met with his full share of personal sorrow. Early in the present century he lost both his sons while they were still lads, and in 1935 his wife died.

Ling served his day and generation well and conferred much of lasting use on the chemical and biological world. THEODORE RENDLE

Some Applications of the Nitro-Ferrocyanide Reaction: A New Formula for Urea

BY W. R. FEARON, M.B., SC.D., F.I.C.

IT has long been known that the sodium nitro-ferrocyanide (nitroprusside) reagent used for the detection of ketones and thiols undergoes a spontaneous oxidation in aqueous solutions exposed to air and light. This change both extends the reactivity and increases the oxidising power of the reagent. For example, the recently prepared reagent gives no immediate colour when added to a guaiacum suspension, whereas the oxidised reagent at once yields a guaiacum-blue pigment.

Similarly, the oxidised reagent in alkaline solution develops an orange-red colour with primary and secondary alcohols, including glycerol, with *p*-cresol, and with urea, guanidine, and their derivatives, none of which compounds gives a colour with the fresh reagent.

The rate and intensity of pigment-formation depend on both the temperature and the state of oxidation of the reagent, and can be increased by addition of an oxidising agent. The reaction was first systematically applied by Tiegs and by Marston, in 1924, and improved by Weber,[9] who introduced the use of a "guanidine reagent," consisting of a mixture of 1 part of 10 per cent. sodium hydroxide solution, 1 part of 10 per cent. sodium nitro-ferrocyanide solution, 1 part of 10 per cent. potassium ferricyanide solution and 9 parts of distilled water. This reagent is very sensitive but of low selectivity, a disadvantage overcome by using Norit to extract the guanidines from solution previous to application of the test (Andes and Myers).[1]

THE SCOPE OF THE NITRO-FERROCYANIDE REACTION.—The following general conclusions have been reached or confirmed during a study of the interaction of both forms of the reagent with some forty different types of compound.

(A) In alkaline solution, a 2 per cent. recently prepared nitro-ferrocyanide reagent yields red or purple pigments with compounds containing (i) an un-ionised thiol group, -SH, or (ii) an enolisable ketone of the system $RH—CO—R' \rightleftharpoons R{=}C(OH)—R'$, where R and R′ are hydrocarbon radicles, one of which, at least, is aliphatic.

Thus: (i) cysteine and glutathione both give a colour, whilst cystine, which occurs in solution as the disulphide -S-S-, does not react; and (ii) both acetone and phenyl-methyl ketone yield typical pigments, whilst diphenyl ketone does not. All these pigments may be formed in presence of either strong alkalis (NaOH) or weak alkalis (NH_4OH), and have the common character of being acid-stable, the tint becoming violet on addition of weak acetic acid.

(B) A related form of the colour reaction is given, under restricted conditions, by ketonoid compounds in which R is an imino group linked on both sides to carbon. These reactions are evoked only in presence of strong alkalis, and the pigments are acid-labile, being bleached at once on addition of acetic acid. Cyanuric acid and creatinine provide examples of this form of the reaction.

Aliphatic aldehydes higher than formaldehyde yield a type A reaction with the reagent, but the colour eventually fades owing to aldol formation. Amides do not react. Monosubstituted hydrazines yield ketones with which they unite to form hydrazones, some of which give a type A reaction (Denigès' test for phenylhydrazine).

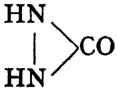
The Nitro-ferrocyanide Reaction with Urea.—Test.—About 5 ml. of a 2 to 3 per cent. aqueous solution of urea is made alkaline by addition of 3 or 4 drops of 10 per cent. sodium hydroxide solution. Ten drops of a 1 per cent. solution of iodine in potassium iodide are added, and the mixture is shaken until the iodine has been bleached to a pale yellow. Then, 3 or 4 drops of a recently prepared 2 per cent. sodium nitro-ferrocyanide solution are added. On standing for a few minutes, the golden-yellow colour of the mixture gradually changes to a ruby-red, which is permanent if sufficient urea is present.

An alternative and more rapid form of the test consists in adding 2 or 3 drops of 2 per cent. potassium persulphate solution to the urea solution, which must not be alkaline, heating the mixture for about half-a-minute, or just to the point of boiling, and then adding the nitro-ferrocyanide reagent, followed by a minimal amount of the alkali. Here, the red colour appears at once, but care must be taken to avoid destruction of the pigment by the alkali. Under controlled conditions this form of the test will reveal urea in concentrations down to about 0·2 per cent. It is inhibited by ammonium salts, which compete with the oxidiser.

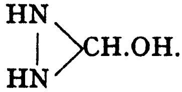
Although the test described above is neither very sensitive nor specific, since it is given by all mono-substituted ureas and guanidines, its importance is due to the light it throws on the structure of urea in solution. Accepting the amidine structure as a possible form in which urea can exist in solution, and the only one likely to react, the obvious point of attack in the molecule is the imino group, and the product is a carbamate.

$$\underset{\text{(amidine form)}}{\underset{\text{Urea}}{HO{-}C(NH){-}NH_2}} \rightarrow \underset{\text{Sodium carbamate}}{NaO{-}CO{-}NH_2 + NH_3}$$

This explanation cannot be correct, since none of the alkaline or other soluble carbamates gives a colour reaction with either the unoxidised or the oxidised reagent. Ethyl carbamate, it is true, develops a pink colour after some hours in contact with the oxidised reagent, but this is due to hydrolytic release of the ethyl alcohol and its conversion into acetaldehyde. This is a type A pigment, and differs from the urea pigment in being acid-stable.

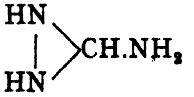
To investigate the problem, a study was made of the products of partial oxidation of urea in weak alkaline solution by bromine and other halogens, ferricyanide, persulphate and peroxide. It is well known that urea in moderately or strongly alkaline solutions is violently attacked by hypobromites, and the mechanism of the reaction has been exhaustively studied by Werner,[10] but if a molecular equivalent of bromine is added to a urea solution of *M* to 10 *M* concentration, and the mixture kept almost neutral by addition of some pieces of calcium carbonate, oxidation proceeds slowly in the cold, with production of a ketonic compound. This ketone can be separated, when the reaction has gone on for some days, preferably in the dark, by distillation of the slightly acidified mixture. All the bromine is removed previous to distillation by acidifying the mixture with 0·1 *N* sulphuric acid and concentrating in a desiccator over sodium hydroxide. The ketone is a colourless liquid with a characteristic smell. It gives an immediate type B reaction with recently prepared nitro-ferrocyanide, and also gives a positive Reynolds reaction (Tognoli).[8] It is rapidly hydrolysed by warm alkalis, and polymerised by strong acids. Heated with barium hydroxide solutions above 60° C., the ketone is quantitatively hydrolysed into hydrazine and carbon dioxide, which implies the formula,  $\begin{matrix}\mathrm{HN}\\ |\\ \mathrm{HN}\end{matrix}\!>\!\mathrm{CO}$, or hydrazi-ketone.

The details of the preparation and properties of hydrazi-ketone will be described elsewhere.

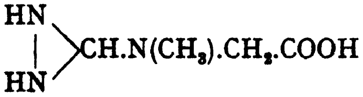
THE STRUCTURE OF UREA IN AQUEOUS SOLUTION.—To account for the oxidative production of hydrazi-ketone from urea the following cyclic formula is proposed, in which urea is represented as hydrazi-carbinol,  $\begin{matrix}\mathrm{HN}\\ |\\ \mathrm{HN}\end{matrix}\!>\!\mathrm{CH.OH}$. This formula also offers an explanation of the properties of urea in aqueous solution, which no current formulae adequately defines. Thus, both the original carbamide formula, $H_2N–CO–NH_2$, and the amidine formula, $H_2N–C(NH)–OH$, indicate the possession of basic properties, which are not shown by solute urea. The dipolar formula first proposed by Werner,[10] $^+H_3N–C(NH)–O^-$, undoubtedly applies to urea in crystalline form (Clow[3]), and to the various reactions undergone by urea in presence of strong acids or alkalis, and appears in all the syntheses of urea so far investigated (Werner, 1923).

In neutral solution, however, urea does not display the properties of a dipolar ion (Wyman,[11] Sidgwick[7]). It has no buffering powers, it does not contain an ionised amino group, $-NH_3^+$, and will only react with nitrous acid in presence of acids strong enough to unmask the latent amino configuration. In 1905, Armstrong and Robertson[2] showed that nitrogen in conjunction with carbon has a preferential tendency to stabilise in three-membered rings, but up to the present time the hydrazi-structure does not appear to have been suggested for urea, although the production of hydrazine when urea is carefully oxidised in alkaline solution has been reported by Schestakoff[6] and by Frankland,[4] and affords evidence of a di-imino linkage in the solute.

According to the theory now advanced, hydrazine arises from the alkaline hydrolysis of the hydrazi-ketone, which is the primary product of urea oxidation. The hydrazi-ring probably occurs in many other compounds containing the amidine system –C(NH)–NH_2, such as guanidine and creatine.



Guanidine



Creatine

Guanidine is a strong base, owing to the presence of the free amino group, but creatine is non-basic in aqueous solution, and thus differs from arginine, in which the amidine group is open. The non-basic character of the amidine group in creatine is inexplicable in terms of the current "open" formula (Hunter[5]). Only when the hydrazi-ring is unlocked by strong acids is its basic character revealed, as happens in the phosphorylation of muscle creatine or the precipitation of urea as the mono-nitrate, HO–C(NH)–$NH_2.HNO_3$.

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DEPARTMENT OF PHYSIOLOGY
TRINITY COLLEGE, DUBLIN

The Iodimetric Determination of Alkali

By G. STANLEY SMITH, B.Sc., A.I.C.

Although the formation of potassium iodide and iodate in the reaction between iodine and potassium hydroxide was discovered as early as 1815 by Sir Humphry Davy, it was not until 1896 that the reaction was applied in analysis for the determination of alkali. In that year Phelps[1] put forward a method for determining carbon dioxide by absorption of the gas in barium hydroxide, which was standardised iodimetrically. Shortly afterwards, in 1899, Walker and Gillespie[2] modified Phelps's procedure and showed how potassium and barium hydroxides might be determined directly, and hydrochloric and sulphuric acids indirectly. More recently an application of the method to the determination of lime in the presence of calcium carbonate has been described by Scott,[3] but most modern text-books of volumetric analysis ignore the method or its applications. It is, however, referred to by Beckurts,[4] and it appears in the 1911 edition of Sutton.[5] The methods of Phelps and of Walker and Gillespie are fully described and discussed by Gooch.[6]

In the method devised by Phelps an excess of $N/10$ iodine was added to a known volume of $N/10$ barium hydroxide solution in a flask fitted with a trap containing potassium iodide solution. After the solution in the flask had been heated to boiling, it was cooled, and the excess of iodine found by titration with $N/10$ arsenite solution. Carbon dioxide was determined by leading the gas into a similar quantity of barium hydroxide in the same apparatus and determining the unchanged hydroxide as before, on the assumption that no observable reaction occurs between barium carbonate and iodine.

The modification introduced by Walker and Gillespie consisted in the determination of the iodate produced by the reaction. The alkaline solution in a conical flask was treated with an excess of $N/10$ iodine solution and gently boiled until all the iodine not required had been expelled, and the volume of the solution had been reduced from about 100 ml. to 35 ml. The solution was then cooled, and, after addition of dilute acid, titrated with thiosulphate, starch being used as indicator. Since alkali carbonates reacted irregularly with iodine, the complete absence of carbonates from the solution was found to be essential to the accuracy of the method. The difficulty of achieving this in practice has undoubtedly interfered with the utility of the process.

The results given in the present paper show that the irregularities observed by Walker and Gillespie when carbonates are present are due to too short a period of reaction and that, by maintaining an excess of iodine in the system for a sufficiently long time, alkali carbonates and bicarbonates, as well as hydroxides, can be accurately determined. The complete transformation of barium carbonate into iodide and iodate is effected in a reasonable time if it has been freshly precipitated. A sample which had been filtered, washed and dried reacted much more slowly with iodine.

In the cold, sodium hydroxide solution dissolves iodine at once, giving a solution containing sodium iodide and sodium hypoiodite.[7]

$$2NaOH + I_2 = NaI + NaIO + H_2O.$$

On standing, but much more rapidly on warming, the hypoiodite is transformed into iodide and iodate.

$$3NaIO = 2NaI + NaIO_3.$$

The complete reaction is represented by the equation

$$6NaOH + 3I_2 = 5NaI + NaIO_3 + 3H_2O.$$

When acid in excess is added to the mixture of iodide and iodate, iodine is set free, exactly equivalent to the amount of sodium hydroxide that had previously reacted with iodine.

$$5NaI + NaIO_3 + 3H_2SO_4 = 3I_2 + 3Na_2SO_4 + 3H_2O.$$

A solution containing iodide and iodate reacts with free acid to give a solution having a *p*H approximately that of the turning-point of phenolphthalein. Kolthoff[8] states that if a solution containing only iodide and iodate is boiled, the reaction even becomes distinctly alkaline to phenolphthalein. If, therefore, sodium hydroxide in solution is completely transformed by iodine into iodide and iodate, the resulting alkalinity should correspond with that of a solution obtained on titrating mineral acid with carbonate-free sodium hydroxide to the phenolphthalein end-point. In actual fact, the alkalinity of the solution, after removal of iodine by boiling, is barely perceptible with phenolphthalein, and may be caused to disappear altogether by the addition of a few ml. of ordinary distilled water (containing carbon dioxide).

Some preliminary experiments on Walker and Gillespie's process were made, with the following results:

(1) 25 ml. of 0·1 *N* NaOH, reasonably free from carbonate, were treated with 25 ml. of water and 50 ml. of 0·1 *N* iodine in KI solution, the iodine was then boiled off, the solution cooled, dilute sulphuric acid added and the iodine liberated titrated with 0·1 *N* thiosulphate. Of this solution, 24·4 ml. were required, as against the theoretical 25 ml. This result was typical of a number obtained similarly. Whenever the solution, after removal of iodine by boiling, was tested with phenolphthalein, the reaction was strongly alkaline.

(2) 25 ml. of 0·1 *N* NaOH were treated with carbon dioxide in excess, the iodine solution was then added and the excess boiled off.
8·0 ml. of 0·1 *N* thiosulphate solution required.

(3) as in (2), except that the solution was boiled for 10 minutes to remove a great part of the carbon dioxide before addition of iodine.
12·1 ml. of 0·1 *N* thiosulphate solution required.

(4) 25 ml. of 0·1 *N* $NaHCO_3$ treated as in (1).
(*a*) 11·3 ml., (*b*) 12·1 ml. of thiosulphate solution required.

(5) 25 ml. of 0·1 *N* Na_2CO_3 treated similarly.
(*a*) 18·3 ml., (*b*) 18·3 ml. of thiosulphate solution required.

Much better results were obtained by repeated additions of iodine over two or three hours, water being added to the gently boiling solution from time to time. In order to avoid the accumulation of potassium iodide, solid iodine was used. Although rather troublesome, this procedure yielded excellent results with sodium carbonate and bicarbonate as well as with the hydroxide. Barium carbonate was found to react to a considerable extent.

The method found most satisfactory and free from difficulty was a reflux process in which benzene was used to prevent the escape of iodine from the reaction mixture. The use of a volatile solvent to retain the iodine in the system was suggested by a paper written by Buehrer and Schupp,[9] who used carbon tetrachloride in a method for determining phosphorus by means of potassium iodate.

The method is carried out as follows:—The alkaline hydroxide or carbonate solution, 2 or 3 ml. of pure benzene and an excess of sublimed iodine are placed in a flask of 150-ml. or 250-ml. capacity, fitted with a ground-in water condenser. The solution is boiled gently until the reaction is judged to be complete, after which the excess of iodine must be expelled. This is most simply effected by continuing the boiling after removing the cooling water from the condenser. Should this treatment cause the flask to adhere firmly, it may usually be removed quite simply by running a little cold water down the condenser to cool the inside of the neck of the flask. The contents of the flask are then cooled and the iodate is determined in the usual manner by means of 0·1 *N* thiosulphate solution, after the addition of potassium iodide and dilute sulphuric acid. Alternatively, without addition of any extra iodide, the acid (preferably about 0·1 *N*) may be added in two stages, the first portion sufficient to produce not more than about a third of the total iodine, which is then nearly removed by the standard thiosulphate, and the second in excess to complete the reaction, followed by titration to the end-point, with starch as indicator.

Some results obtained by this method are given below. The sodium thiosulphate solution was standardised against potassium iodate and potassium bromate. The alkali solutions were standardised against 0·1 *N* sulphuric acid, itself standardised against pure sodium carbonate. Phenolphthalein and rosolic acid were used as indicators in these neutralisation titrations, which were finished after complete removal of carbon dioxide. Incidentally, the use of rosolic acid can be highly recommended for titrations in boiling solution, as the end-point can be observed very accurately, even with 0·01 *N* solutions.

(1) *Sodium hydroxide.*—25·0 ml. of 0·1 *N* sodium hydroxide solution, refluxed for 20 minutes, required 25·0 ml. of 0·1 *N* thiosulphate solution. 50 ml. of 0·1 *N* sodium hydroxide solution, refluxed for 30 minutes, required 50·0 ml. of 0·1 *N* thiosulphate solution.

Identical results were arrived at when the time of refluxing was increased to one, two or three hours.

(2) *Sodium carbonate.*—25·0 ml. of 0·1 *N* sodium carbonate solution, refluxed for 2½ hours, required 25·0 ml. The reaction was never quite complete in 2 hours.

10 ml. of 0·01 *N* sodium carbonate solution, refluxed for one hour, required 9·7 ml. of 0·01 *N* thiosulphate solution.

(3) *Sodium bicarbonate.*—With 25·0 ml. of 0·1 *N* solution exact results were obtained, but only after about three hours.

(4) *Barium carbonate.*—(*a*) *Precipitated, filtered, washed and dried.*—The product was well mixed and similar amounts taken for the iodine treatment and for titration with standard acid. 0·2468 g. was found to be equivalent to 25·1 ml. of 0·1 *N* hydrochloric acid. The same quantity, after being refluxed for three hours with iodine, produced three quarters of the theoretical amount of iodate.

0·1 *N* thiosulphate solution required = 18·5 ml.

Another portion, refluxed for nine hours, required 23·9 ml.

(*b*) *Freshly precipitated.*—25·0 ml. of 0·1 *N* barium hydroxide solution were treated with carbon dioxide gas in excess, and after the addition of 50 ml. of water, followed by iodine and benzene, boiled under a reflux condenser. The solution remained cloudy, showing the presence of barium carbonate, for nearly two hours, when it became perfectly clear. The heating was continued for another hour, after which the iodine was expelled, the solution cooled, and potassium iodide and hydrochloric acid were added, and the iodine liberated was titrated with thiosulphate. The theoretical quantity (25·0 ml.) was required.

Barium hydroxide, treated in the same way, without carbon dioxide, gave the same result.

(5) *Calcium carbonate, precipitated, washed and dried.*—0·1251 g., equivalent to 24·7 ml. of 0·1 *N* hydrochloric acid, after being refluxed for five hours with iodine, required 17·8 ml. of thiosulphate solution instead of the theoretical 24·7 ml.

The method provides a direct comparison of standard alkali with standard thiosulphate solution. It may be mentioned that there is another method available for the direct comparison. This depends upon the titration of the acid liberated in the reaction between thiosulphate and mercuric chloride, and has been investigated by Wöber, by Bodnar and by Sander (references in Kolthoff[10]).

The excellent results obtainable with sodium carbonate would warrant the use of this substance as an iodimetric standard. Although the time required for complete transformation into iodide and iodate is somewhat long, the apparatus needs no attention.

A further development was achieved by determining the amount of iodide in the solution after the thiosulphate titration. It was found possible to titrate the iodide with 0·1 *N* silver nitrate solution, with the use of an adsorption indicator. For this purpose the thiosulphate titration was preceded by the addition of acid in two stages, so that, in the absence of an excess of potassium iodide, the free iodine should not separate from the solution. After the exact end-point with thiosulphate had been obtained the solution was neutralised (with dilute alkali and sulphuric acid) to methyl orange, a few drops of the adsorption indicator were added, and the iodide was titrated with silver nitrate. The volume of the silver solution required agreed, within 0·05 ml., with that of the thiosulphate previously used. As adsorption indicator a red writing ink diluted 10-fold was found suitable.[11]

Hence it is possible to use sodium carbonate as a standard in alkalimetry, iodimetry and argentometry.

DETERMINATION OF IODATE AFTER REMOVAL OF FREE IODINE BY MEANS OF PHENOL, AND ITS APPLICATION TO THE DETERMINATION OF ALKALI.—In the method described above the excess of iodine at the end of the reaction is removed by boiling. If only a slight excess of iodine has been added originally, a few minutes suffices for this operation, but as much as half-an-hour may be necessary at times. In any event, it is impossible to discover the extent of conversion after any given time unless the iodine can be removed by some means other than boiling. As an alternative, the possibility of using phenol to bind the iodine was considered.

Gardner and Hodgson[12] found that phenol might be quantitatively determined by means of iodine, if, after addition of excess of iodine, dilute alkali were added in amount just sufficient to decolorise the solution; then, after acidification of the solution, the excess of iodine was titrated with thiosulphate solution. They remarked that excess of alkali was injurious.

Under these conditions one atom of iodine is required for each molecule of phenol. The compound formed is colourless and soluble in water.

Cofman[13] also studied the reaction between phenol and iodine in the form of alkali hypoiodite. He found that if excess of phenol were added to an iodine solution previously treated with alkali, so that, in addition to hypoiodite, some iodate was present, the hypoiodite reacted, but not the iodate. The iodate could be determined by titration with thiosulphate after acidification with acetic acid. The use of a strong mineral acid was stated to be objectionable, since, before the hydroxide can be completely neutralised, the acid liberates iodine from some of the iodide and iodate, and this iodine is partly transformed into hypoiodite, which reacts at once with phenol and does not show in the subsequent titration.

Schulek[14] also emphasised the necessity for careful removal of hydroxyl ions before acidification. This may be done by means of carbon dioxide (*cf.* Batey[15]).

In acid solution no reaction occurs between phenol and free iodine, potassium iodide or potassium iodate; in neutral solution, moreover, phenol is incapable of liberating iodine from a mixture of iodide and iodate; in alkaline solution phenol is not attacked except by hypoiodite. In the experiments on which these conclusions are based sulphuric acid was used to acidify the solution prior to the titration, but the effect noted by Cofman was observed only when comparatively large amounts of alkali had to be neutralised. Under such conditions approximately correct results were obtained when acetic acid was substituted for sulphuric acid. For lower alkalinities, sulphuric acid may be used without introducing any error.

Solutions used.—Potassium iodate, 0·1 *N* solution; sodium thiosulphate, 0·1 *N* solution; potassium iodide, 10 per cent. solution; iodine, 4 per cent. in 10 per cent. potassium iodide solution; phenol, 5 per cent. aqueous solution; sodium hydroxide, approx. 0·5 *N* solution; sulphuric acid, dilute (sp.gr. 1·2).

Procedure.—The solution of the composition indicated in Table I was treated with 5 ml. of phenol solution, the specified amount of sodium hydroxide solution was added, followed, after a few seconds, by 10 to 15 ml. of dilute sulphuric acid, and the liberated iodine was titrated with thiosulphate solution, starch being used as indicator. Potassium iodide was added, if necessary. The quantity of sodium hydroxide solution used was at least sufficient to decolorise the solution in those experiments in which free iodine was present. The volume of the solution before titration was approximately 100 ml.

TABLE I

Composition of solution				
Potassium iodate ml.	Potassium iodide ml.	Iodine ml.	Sodium hydroxide sol., 0·5 *N* ml.	Thiosulphate solution required ml.
nil	10	—	nil	nil
nil	10	—	25	nil
nil	—	5	10	nil
25·0	—	—	nil	25·0
25·0	—	—	15 ml. of 5 *N*	25·0
25·0	10	—	nil	25·0
25·0	10	—	5	25·0
25·0	10	—	10	24·5
25·0	10	—	25	23·6
25·0	10	—	8 ml. of 5 *N*	22·5
25·0	—	5	2	25·0
25·0	—	5	5	25·0
25·0	—	5	10	24·5

The modification in the iodimetric determination of alkali suggested by the results given above is as follows:—After the alkaline solution has been refluxed

TABLE II

			Thiosulphate solution, 0·1 *N*	
Alkali	Volume of solution refluxed ml.	Duration of refluxing Minutes	Calculated ml.	Found ml.
NaOH, 0·1 *N*				
20·0 ml.	70	5	20·0	19·85
20·0 ,,	70	10	20·0	19·9
20·0 ,,	70	20	20·0	20·0
50·0 ,,	70	30	50·0	50·0
Na_2CO_3, 0·1 *N*				
25·0 ml.	70	10	25·0	18·0
25·0 ,,	70	45	25·0	21·6; 22·1
25·0 ,,	70	60	25·0	23·7
25·0 ,,	70	120	25·0	24·8; 24·9
25·0 ,,	70	180	25·0	25·0; 25·0
Borax				
0·3814 g.	70	5	20·0	18·8
Do.	70	30	20·0	19·0
Do.	70	90	20·0	18·8
Do.	500	30	20·0	19·7
0·9538 g.	70	30	50·0	45·4
Do.	70	45	50·0	37·5
Sodium aluminate	70	90	25·0	24·95
Sodium silicate	70	90	25·0	25·0

with iodine in benzene for a sufficient time, cool the solution, now containing iodide and iodate, add 5 ml. of 5 per cent. phenol, and run in 0·1 *N* sodium hydroxide solution, with shaking, until all trace of iodine colour is removed. Then add an excess of potassium iodide and dilute sulphuric acid and titrate with thiosulphate.

Some typical results, so obtained, are shown in Table II.

The sodium aluminate solution was obtained by dissolving 0·05 g. of aluminium in 25·0 ml. of 0·1 *N* sodium hydroxide solution.

The sodium silicate solution was a solution of the salt standardised by titration against 0·1 *N* sulphuric acid.

The figures confirm the previous results for sodium hydroxide and carbonate, and indicate that the alkali of sodium aluminate and silicate, but not that of sodium borate, may be quantitatively determined by the iodimetric process described.

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The Micro-Determination of Gold

By W. B. POLLARD, B.A., Ph.D., F.I.C.

INTRODUCTION.—In previous papers[1,2] I have investigated micro and macro methods for the volumetric determination of gold, and in the present paper I have attempted to develop a technique for the determination of traces of gold in solution, similar to that which has long been used for ores.

The therapeutic use of gold preparations has led to a demand by the medical profession for micro methods for studying the elimination of gold. In the course of this investigation a "collector" has been found, by the use of which gold can be co-precipitated from very dilute solution; this acts in the "wet" assay as lead does in the dry. With this "collector" it has been found possible to recover almost spectroscopic amounts of gold from solution without recourse to evaporation.

PREPARATION OF GOLD SOLUTIONS FOR TITRATION.—The first step in the volumetric determination of gold is its conversion into chloroauric acid or the analogous bromine compound.

Precipitated gold, or gold resulting from "parting" an alloy in nitric acid, can be dissolved in bromine water acidified with hydrochloric acid, but gold that has been melted or strongly heated is more easily dissolved in *aqua regia.*

In whichever way the gold has been dissolved, the solution must be freed completely from nitrosyl chloride, chlorine or bromine before titration. Evaporation to dryness on the water-bath cannot be employed, owing to the partial loss of chlorine from chloroauric acid, but this does not occur when these substances are removed by the passage of a current of air through the liquid.

Aqua-regia solutions, obtained by dissolving small amounts of gold in 2 drops of nitric and 6 drops of hydrochloric acid in a porcelain crucible, are freed from gases by allowing a stream of air to impinge on the surface of the acid. This can be done by placing the crucible in a 150-ml. beaker which can be closed by a rubber cork, as shown in the diagram (Fig. 1). Through the centre of the cork passes a short length of glass tube, of about 1·5 mm. bore, down nearly to the level of the crucible. Another tube also passes through the cork and can be connected with the vacuum water-pump by means of a rubber tube.

On starting the pump air is drawn through the centre tube and impinges on the *aqua regia* contained in the crucible, and after two or three minutes the gases will have been removed. After this air treatment 50 ml. of water are put in the beaker, together with the crucible, and the solution is then ready for titration.

If gold is alloyed with more than twice its weight of a base metal, it can generally be "parted" by heating it in a test-tube with nitric acid of sp.gr. 1·2. The gold is then separated from the nitric acid solution by means of the filtering device shown in Fig. 2.

This consists of a piece of capillary tubing (1 mm. bore), with a double right-angle bend. At the end of the long arm a small bulb is blown. An opening is also blown at the top of the bulb, so as to form a small thistle-funnel, and into this is pushed a plug of asbestos wool to serve as a filtering medium. The short arm

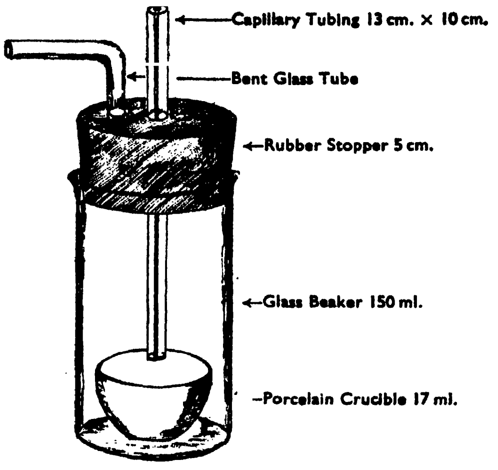
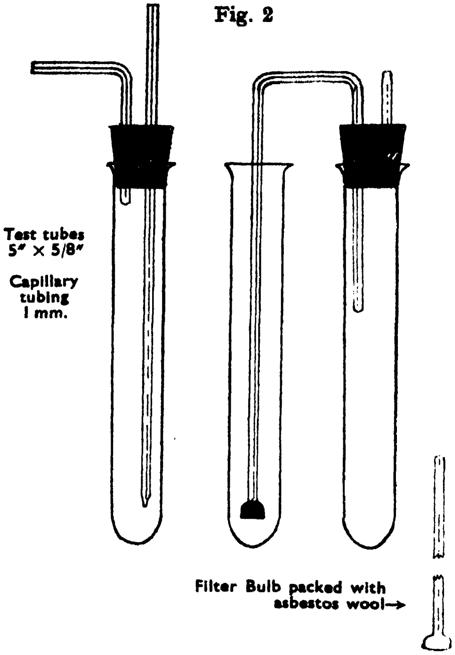


Fig. 1

Fig. 2



passes through a rubber cork which can be inserted in a test-tube. A short length of glass tube also passes through the rubber cork and can be connected by means of a rubber tube with the vacuum water-pump.

The filter is inserted down to the bottom of the test-tube containing the "parted" gold, and the nitric acid is drawn over into the second test-tube, which is connected with the water-pump. The sides of the first tube are washed down two or three times with water. The test-tube containing the nitric acid is then removed and replaced by an empty tube. Ten ml. of saturated bromine water and 2 drops of hydrochloric acid are added to the tube containing the gold and, when this has dissolved, gentle suction is applied, and the bromine water is transferred to the empty tube. Suction is increased, and the sides of the first tube are washed down two or three times with water. The tube, which now contains the gold as bromoauric acid with excess of bromine water, is disconnected from the filter.

To remove the bromine, a rubber cork, through which pass two glass tubes, is inserted in the test-tube, as shown in Fig. 2. The longer tube passes to within a centimetre of the bottom of the test-tube and terminates in a fine jet. The short tube is connected with the vacuum-pump by means of a rubber tube. When the pump is started a turbulent jet of air is drawn through the solution and the bromine is quickly removed. By adjusting the size of the jet at the end of the tube any danger of sucking over the gold solution is avoided. The time required to remove the bromine from 10 ml. of saturated bromine water is approximately 2½ minutes. In actual practice double this time is always allowed. Under altered conditions the exit air can always be tested by passage through a second tube containing a little of the *o*-dianisidine indicator described below, which will show a pink colour with minute traces of bromine and chlorine. The gold solution is then transferred to a beaker and is ready for titration.

Gold can be separated from almost every impurity by precipitation with a suitable reducing agent. After precipitation of the gold in a test-tube, the asbestos micro-filter can be inserted, and the gold collected and washed. Precipitated gold dissolves very quickly in bromine water acidified with 2 drops of hydrochloric acid. By sucking the bromine solution slowly through the filter, the gold is almost instantly dissolved. The filter can be washed with distilled water, and the solution freed from bromine as described above.

THE MICRO-TITRATION OF GOLD.—The method previously described by me (*loc. cit.*) depended on the conversion of gold into the tervalent condition, followed by reduction to metallic gold by a standard reducing agent. At first *o*-tolidine was used as indicator, but this was afterwards replaced by *o*-dianisidine, which was found to be more reactive. Chloroauric acid forms an intense reddish compound with this substance in faintly acid solution. The addition of a standard hydroquinone solution precipitates metallic gold and at the same time discharges the colour.

The *p*H of the solution plays an important part in the titration. If it lies too much on the acid side, combination between the chloroauric acid and *o*-dianisidine is retarded, and it is necessary to wait for the re-formation of the colour before the titration can be continued. If the *p*H moves too far towards the alkaline side, a sparingly soluble compound tends to separate. Both these defects can be overcome by the use of acid potassium fluoride as a buffer.

The reduction of chloroauric acid with hydroquinone proceeds according to the equation:

$$2HAuCl_4 + 3C_6H_6O_2 = 2Au + 3C_6H_4O_2 + 8HCl.$$

The solutions required are prepared as follows:

Standard Hydroquinone Solution.—0·4186 g. of pure hydroquinone is dissolved in about 200 ml. of water, 10 ml. of hydrochloric acid are added, and the volume is made up to 500 ml. (1 ml. of solution ≡ 1 mg. of gold).

Standard Gold Solution.—0·5 g. of pure gold is dissolved in a 500-ml. flask by gently warming it with 2 ml. of nitric acid and 6 ml. of hydrochloric acid. Dissolved gases are removed from the solution by inserting a glass tube into the liquid and blowing in a strong current of air for about five minutes. Liquid adhering to the tube is washed into the flask, the tube is removed, and the volume is made up to 500 ml.

o-Dianisidine indicator solution.—0·5 g. of *o*-dianisidine is dissolved in 200 ml. of water and 2 ml. of hydrochloric acid and put in a 500-ml. standard flask, and the solution is made up to 500 ml.

The relation between the gold and hydroquinone solutions was determined as follows:

Various amounts of gold solution were transferred by means of a 2-ml. pipette into 50 ml. of distilled water, and 2 drops of strong hydrochloric acid were added. The solution was buffered with acid potassium fluoride, 1 ml. of indicator solution was added, and, without waiting, standard hydroquinone solution was run in from a micro-burette graduated in hundredths of a ml. until the red colour was just discharged.

The operation was then repeated, but this time the indicator was not added until the hydroquinone solution had been run in to within 0·05 ml. of the amount used in the first titration. After a short delay for the colour to develop, the titration was finished as before. The results of the two methods of titration are recorded below:

Gold solution taken ml.	Hydroquinone used with indicator at start ml.	Hydroquinone used with indicator at end ml.
2·0	1·98	1·99
2·0	1·97	2·00
2·0	1·98	2·00
1·0	0·98	0·99
1·0	0·98	0·99
0·5	0·50	0·50
0·5	0·49	0·50
0·2	0·20	0·20
0·2	0·20	0·20

The slight difference in the two series of titrations is probably due to the gradual fading of the red colour, which occurs when solutions are left standing. The first method of titration is the one that would normally be adopted; the second can be used only when the results are known within narrow limits.

The strength of the hydroquinone solution remains unchanged for several months, but in time the solution develops a slight brown colour. Hydroquinone can be obtained in a sufficient degree of purity to enable a standard solution to be made up directly.

The method is essentially a micro one, and is most suited to quantities of less than 2 mg. of gold. If larger amounts of gold are taken, the second method of titration should be used. The indicator should not be added until less than 2 mg. of gold remain in solution.

THE EFFECT OF OTHER METALS ON THE TITRATION.—The effect of other metals was tested by dissolving 10 mg. of the metal in 2 drops of nitric acid and 6 drops of hydrochloric acid in a porcelain crucible. In the tests with lead and silver the metal was dissolved first in the nitric acid and afterwards the hydrochloric acid was added. The solutions were blown with air in the manner already described, and diluted with 50 ml. of water, and then 2 ml. of the standard gold solution were added. The solution was buffered with acid potassium fluoride, 1 ml. of indicator solution was added and, without delay, the liquid was titrated.

Metal taken	Gold taken mg.	Gold found mg.
10 mg. of copper	2	1·99
10 mg. of silver	2	2·01
10 mg. of iron	2	2·00
10 mg. of nickel	2	2·00
10 mg. of zinc	2	2·03
10 mg. of cadmium	2	2·03
10 mg. of aluminium	2	1·97
10 mg. of tin	2	2·07
10 mg. of lead	2	2·54

The error that results when lead is present can be eliminated if the *aqua-regia* solution is diluted and a few drops of bromine water added, and the excess of bromine removed by the passage of air through the solution. Correct values are then obtained in the titration. In strong *aqua-regia* solutions lead appears to form a higher chloride which breaks down on addition of water, with the liberation of free chlorine.

When large amounts of metallic impurities are present the gold should be separated before attempting the titration. A large number of reducing agents are available, but some of them are not very satisfactory when used in micro-determinations.

Stannous chloride gave excellent results with *aqua-regia* solutions. As nitric acid was converted into ammonia, it was not necessary to remove this substance before precipitating the gold—

$$2HNO_3 + 8SnCl_2 + 18HCl = 7SnCl_4 + (NH_4)_2SnCl_6 + 6H_2O$$

The reaction should be carried out just below the b.p. in strong hydrochloric acid solution, and under these conditions the gold is precipitated as metal and not as "purple of Cassius." The stannous chloride solution was prepared by dissolving 200 g. of the salt in 100 ml. of strong hydrochloric acid and was filtered through asbestos wool. It does not precipitate the platinum metals unless mercury, arsenic, tellurium or selenium is also present. By a second precipitation with "metol" or *p*-phenylenediamine hydrochloride, the gold can be obtained free from these impurities. Precipitants such as oxalic acid which react slowly, were not found as satisfactory as those with a high velocity of reaction. Direct precipitation is only advisable when dealing with small volumes of solution; when the gold has to be separated from metallic impurities in large volumes of solution, concentration by co-precipitation should be employed.

CO-PRECIPITATION OF GOLD WITH TELLURIUM.—Gold is known to precipitate with tellurium from solutions that contain from 10 to 42 per cent. by vol. of strong hydrochloric acid, and the passage of sulphur dioxide through such solutions precipitates the tellurium in a form in which it can be readily filtered. Large volumes of liquid can be passed through the most rapid filters while every trace of tellurium is retained.

Mercury, platinum, palladium and selenium, and small amounts of titanium, tin, antimony, bismuth, molybdenum, etc., are, as is known, carried down with the tellurium. Barium, strontium and lead would precipitate as sulphates, but could be removed before precipitating the tellurium.

To test the possibilities of tellurium as a "collector" for gold, a solution was prepared by dissolving 5 g. of powdered tellurium in 20 ml. of hydrochloric acid and 5 ml. of nitric acid in a beaker on the water-bath. Nitric acid was then removed by evaporating the liquid to a thick syrup after addition of hydrochloric acid. Twenty-five ml. of hydrochloric acid were added, and the volume was made up to 50 ml. with distilled water. Each ml. of solution thus contained 100 mg. of tellurium.

Blank tests were made first with 10 litres of tap water alone, and then with the addition of known amounts of a standard chloroauric acid solution. It was found necessary to add 1 litre of strong hydrochloric acid to each 10-litre sample, as sulphur dioxide failed to precipitate the tellurium when less was used. After acidification, 2 ml. of tellurium solution were added, the sulphur dioxide was passed into the well-mixed solution, until there was a strong odour of the gas. The containing vessel was then left on the water-bath overnight.

The liquid was filtered through a Buchner funnel. The paper and precipitate were transferred to a 17-ml. porcelain crucible, charred at a low temperature, burnt off at a rather higher temperature, and finally heated strongly for a few minutes. During the burning most of the tellurium escaped, but a little dioxide was left in the crucible.

When the crucible was cold, 6 drops of hydrochloric acid and 2 drops of nitric acid were added, and any undissolved solid was broken up with a short piece of glass rod. The crucible and rod were then placed on the top of the water-bath for 15 minutes, and the gold was dissolved. The crucible was not placed directly in the steam, as this caused too rapid evaporation. After air-treatment the solution was diluted, buffered and titrated in the usual way. The following results were obtained:

Gold determined in 10 litres of tap water acidified with 1 litre of hydrochloric acid

No.	Gold present mg.	Tellurium added mg.	Gold found mg.
1	none	200	none
2	none	200	none
3	0·01	200	0·01
4	0·02	200	0·02
5	0·05	200	0·05
6	0·10	200	0·10

The method will therefore recover one part of gold in a thousand million parts of solution.

In order to test the effect of metallic impurities on the recovery of gold by co-precipitation with tellurium, a solution was made containing 1 g. each of the chlorides of calcium, magnesium, aluminium, iron, zinc, cadmium, bismuth and copper dissolved in 100 ml. of 10 per cent. hydrochloric acid. To this 1 ml. of standard gold solution and 1 ml. of tellurium solution were added. The tellurium and gold were then precipitated with sulphur dioxide and the gold was titrated. In two experiments 0·99 mg. of gold was recovered as compared with 1·00 mg. taken.

As palladium is carried down by tellurium and interferes with the gold titration, search was made for a reagent that would precipitate gold without also precipitating tellurium and palladium. "Metol" and *p*-phenylenediamine both seem to have the required properties. In the following test the gold was precipitated in dilute hydrochloric acid solution at the boiling-point. The gold was collected on the micro-filter, washed, dissolved in bromine, and titrated in the usual way.

Gold taken mg.	Palladium mg.	Platinum mg.	Tellurium mg.	Gold found mg.	Precipitant
1·00	1·00	—	20·00	0·99	"Metol"
2·00	1·00	1·00	20·00	1·98	,,
0·50	1·00	—	20·00	0·49	,,
0·50	1·00	—	20·00	0·50	*p*-phenylenediamine hydrochloride

Co-precipitation with tellurium was found to be a rapid method for the determination of gold in the urine of persons who were undergoing treatment with gold salts. The gold could also be completely recovered from solutions of the complex gold salts used in the treatment.

I wish to express my thanks to Sir Harold Carpenter for the facilities provided.

REFERENCES

1. W. B. Pollard, *Trans. Inst. M. M.*, 1923, **32**, 242.
2. —— *Id.*, 1932, **41**, 434.

ROYAL SCHOOL OF MINES
LONDON, S.W.7

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A NEW COLORIMETRIC TEST FOR NOVOCAINE AND PRIMARY AMINES

NOVOCAINE, like all primary amines, gives an immediate colour when treated with a solution of paradimethylamino-benzaldehyde in presence of hydrochloric acid. A drop or a minute particle of the primary amine to be tested is treated on a slide with a drop of the aldehyde solution (prepared by dissolving 4 g. of the aldehyde in 380 ml. of absolute alcohol and 80 ml. of conc. hydrochloric acid). Primary amines generally give a yellow, greenish-yellow or orange colour, undoubtedly due to the formation of coloured dye (Schiff's) bases.

This test, which has obvious advantages over the diazo test for primary amines, should prove particularly valuable in analytical laboratories where hundreds of samples have to be tested every year for the presence of novocaine. One of the usual adulterants of cocaine in India is novocaine, and novocaine is at once indicated by the greenish-yellow colour obtained, whereas the other usual adulterants, such as acetanilide, aspirin, starch, eucaine, alypin, antipyrine, aconitine, apomorphine, atropine, caffeine, tropacocaine and scopolamine, and cocaine itself give no colour. Orthoform and anaesthesin give a greenish-yellow colour, but novocaine is easily distinguished from these compounds. Commercial novocaine (hydrochloride) is completely soluble in water, whilst orthoform and anaesthesin are insoluble.

During the last ten years several tests for novocaine have been suggested (*e.g.* Young, *Amer. J. Pharm.*, 1931, **103**, 709; Abst., ANALYST, 1932, **57**, 179; Wagenaar, *Pharm. Weekblad.*, 1932, **69**, 727; Abst., ANALYST, 1932, **57**, 579; Wagenaar, *Mikrochem.*, 1932, **12**, 143; Abst., ANALYST, 1933, **58**, 178; Sanchez, *Ann. Chim. anal.*, 1934, **16**, 249; Abst., ANALYST, 1934, **59**, 634), but none of these is so simple or definite as that we have described.

S. N. CHAKRAVARTI
M. B. ROY

CHEMICAL EXAMINER'S LABORATORY
AGRA, INDIA

ANALYTICAL DATA ON PALESTINIAN OLIVES AND OLIVE OIL

THE analytical results obtained in the examination of samples of olives from ten trees, over a period of four years (1933–1936) may be summarised as follows:

Years	1933	1934	1935	1936
Average weight of each olive (grams)	1·74	2·60	1·98	2·07
Proportion of seed to flesh (flesh = 1)	0·41	0·27	0·33	0·33
Analysis of the flesh				
Water, per cent.	41·9	42·6	39·9	37·7
Oil, per cent.	34·7	38·8	36·3	40·8
Oil (calculated on dry sample), per cent.	59·9	67·6	59·4	65·5
Ash, per cent.	1·56	1·20	1·46	1·15
Protein ($N \times 6{\cdot}25$), per cent.	1·59	1·78	1·94	2·07

Experiments on the acidity of local olive oil.

(*a*) Selected olives. Per Cent.
- (1) Picked by hand = 0·3
- (2) Combed = 0·3
- (3) Beaten in usual way = 0·3

(*b*) Average whole sample.
- (1) Picked by hand = 0·45
- (2) Combed = 0·55
- (3) Beaten in usual way = 0·90

(*c*) Acidity of oil pressed after keeping olives 10 days.
Per Cent.
- (1) Picked by hand = 1·4
- (2) Combed = 1·65
- (3) Beaten in usual way = 2·15

(*d*) Oil from local presses 3 to 10 per cent.

The acidity of local olive oil varies (as shown above) according to the methods of gathering, handling and pressing. The practice of gathering by beating the tree, stacking the olives in heaps for 10 days prior to pressing, and the use of primitive hand-presses all tend to increase the acidity by fermentation. The best unrectified edible oil on the local market has an acidity of 3 to 5 per cent., whilst that from some of the more primitive presses may contain 10 per cent. or more. Oil pressed in the laboratory from selected hand-picked olives contained 0·3 per cent. of acid. In the same olives after being kept for 10 days the acidity had risen to 1·4 per cent. In unselected olives, harvested by beating, an initial acidity of 0·9 per cent. rose in 10 days to 2·15 per cent.

The analytical values obtained by W. Zananiri in these laboratories on ten samples from different local presses were as follows:

	Sp.gr. at 15°C.	Saponification value	Reichert–Meissl value	Iodine Value (Hübl)	n_D^{25}
Minimum	0·911	183·7	0·77	81·0	1·4670
Maximum	0·918	193·5	0·99	84·7	1·4680
Average	0·915	189·3	0·83	82·6	1·4675

G. W. BAKER
M. PUFFELES

GOVERNMENT CENTRAL LABORATORIES
JERUSALEM

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ARTIFICIAL VINEGAR SOLD AS "TABLE VINEGAR"

SUTTON *v.* TAME

ON June 15th Mr. Eustace Fulton, Chairman of the County of London Sessions Appeal Committee, heard an appeal against a fine imposed by Sir Rollo Graham-Campbell, at Bow Street Police Court, for selling vinegar not of the nature, substance and quality demanded by the purchaser (see ANALYST, 1937, 384).

The respondents to the appeal were the Westminster City Council, who were represented by Mr. St. John Hutchinson, K.C., and Mr. Vernon Gattie. The appellant was represented by Mr. Kenneth Swan, K.C., and Mr. R. E. L. Parry.

In reply to the Chairman's enquiry, Mr. Swan said that the point to be decided was whether there was any significance in the term "table vinegar." It was his contention that that term had been applied to a substance for many years, and was a correct and proper description.

Mr. Hutchinson said that the Westminster City Council contended that for a substance to be called "vinegar" at all it should be brewed. The certificate of the Public Analyst showed that the substance in question consisted of 100 per cent. of artificial vinegar. The Council contended that vinegar must be a product brewed from malt, whereas the substance they complained of was really synthetic and was made up of acetic acid and water together with some colouring. It was not brewed at all, which, they were contending, was an essential feature of vinegar. There was a great difference in the process of manufacture and undoubtedly a great difference in taste. The general trade looked upon brewed vinegar as a different article. For over 300 years vinegar had been made by fermentation, and their contention was that one could not change the whole attitude of the people towards a substance by manufacturing it later in a synthetic manner. They felt that if people were going to get that sort of manufactured vinegar there ought to be some notice upon it, so that they knew what they were buying.

Mr. F. W. Edwards, Public Analyst for Westminster, said that, in his view, fermentation was an essential part in the manufacture of vinegar. Artificial vinegar did not contain any mineral salts, proteins or vitamins, and the odour and taste were utterly different from those of genuine vinegar.

In cross-examination the witness said that there were no chemical operations in the manufacture of brewed vinegar; they were all biological. He agreed, however, that malt vinegar had to be manufactured by a sequence of carefully controlled steps. Real vinegar could not be produced from wood, although for many years there had been a substance known in the trade as "wood vinegar." There were very few Public Analysts in this country who refused to condemn wood vinegar if sold as vinegar.

Dr. C. Ainsworth Mitchell said that, in his opinion, vinegar ought to be defined with reference to its source. He would accept "imitation vinegar" as a proper description of wood vinegar, but would not accept "vinegarine." From his knowledge of the trade he was of opinion that they accepted the definition put forward by Dr. Hamill (now of the Ministry of Health) in his Report to the Local Government Board. He did not consider that the word "table" defined wood vinegar.

In cross-examination the witness agreed that Dr. Hamill's recommendation to the Local Government Board had not been adopted by the Ministry of Health.

Dr. H. E. Cox, Public Analyst for Hampstead and for Cornwall, said that he agreed with the definition of vinegar that had been drawn up by the Society of Public Analysts (*cf.* ANALYST, 1935, 60, 3). He had not heard that any protest against that definition had been sent by any member of the Society. He would not accept "table vinegar" as a correct description of "wood vinegar"; there had been numerous prosecutions for the sale of artificial vinegar as "vinegar" or "table vinegar."

Evidence was then given by several representatives of large firms of grocers and provision merchants to the effect that they sold only brewed malt vinegar, and that if asked for "vinegar" they would not supply artificial vinegar.

For the appellant, trade evidence was called to prove that there was an extensive trade done in acetic acid vinegar, and that, although the product was made by different firms, it had for many years been sold as "table vinegar."

When the Court resumed on June 16th, Mr. Swan called scientific evidence on behalf of the appellant.

Dr. E. J. Parry said that, in his opinion, the word "vinegar" did not connote merely a brewed condiment, and "table vinegar" was to him an expression for pure vinegar. He regarded non-fermented vinegar as pure vinegar in the ordinary sense of the word. The vinegar to which he referred as "factitious" in 1910 was the imitation malt vinegar made by adding phosphates and proteins to diluted acetic acid and so deceiving the analyst.

In cross-examination, Dr. Parry said that he did not think that one in a thousand members of the public knew the difference between brewed and non-brewed vinegar, but he agreed that the public should know what they were buying.

Mr. William Lincoln Sutton, Public Analyst for Norfolk and Suffolk, said that the trade description of malt vinegar was generally "malt," but he had known the unbrewed product to be sold as "vinegar," and occasionally as "table vinegar." He thought that the definition of vinegar formulated by the Society of Public Analysts was too restricted.

Mr. A. J. Lickorish, Public Analyst for the City of London, who attended on subpoena, said that so long as vinegar was not labelled "malt vinegar" he saw no reason why the acetic type should not be sold as "vinegar" or "table vinegar."

In reply to the Chairman's question, whether a customer ought not to know what he was buying, the witness replied that he would know from the label; if the customer were having his own bottle filled, he would know by the flavour. If he (the witness) went into a shop and asked merely for "vinegar," he would expect to get synthetic vinegar.

Mr. Swan, addressing the Committee, said that there was no legal standard for vinegar, although various attempts had been made to get one. Bills had been promoted in Parliament to put the matter on a proper footing, but they had lapsed. During the last 25 or 30 years vinegar from wood and other synthetic sources had been evolved, and acetic acid had been produced in a state of great purity. He contended that the Statute was never designed to decide a question of this nature. A most extensive practice in non-brewed vinegar had been built up, and it was only in the past five or six years that the manufacturers had added words to inform the public whether it was brewed or non-brewed. The question his lordship had to decide was: "Does the expression 'table vinegar' necessarily mean malt or brewed vinegar?" It was essential in the case of a penal statute that it should mean "necessarily." An article demanded meant an article commercially known under that name. He asked the Committee to find as a fact that the public had, for a considerable number of years, asked for and bought this quality of vinegar by the name "vinegar" and by the name "table vinegar." The term "vinegar" might mean one of many things and, in his submission, if a customer asked for vinegar, it could not be suggested that he did not receive what was demanded if supplied with the non-brewed variety. There was abundant evidence of a differentiation in trade terminology with regard to the description of non-brewed vinegar. It would be unfair to conclude that when a purchaser went to a shop and asked for table vinegar, by which name millions of bottles had been sold to the public, that he only meant that he wanted malt vinegar.

The Chairman, announcing the decision of the Committee, said: "The Committee desire to thank counsel on both sides and the expert witnesses on both sides for the very valuable assistance they have given them in arriving at a decision in this rather difficult case. The Committee cannot agree with Mr. Swan's contention that the words 'table vinegar' have become a term of art and are, by a custom of the trade, in this case used to denote what may be termed synthetic vinegar. The fact that a very large majority of manufacturers add such words as 'wood,' 'non-brewed,' or similar words of that description to the products, shows, in the opinion of the Committee, that the words 'table vinegar' are not considered by the custom of the trade sufficient to describe it. The Committee are satisfied on the evidence that to sell a substance as 'vinegar' or 'table vinegar' without any qualification or explanation as to its origin being given by the seller to the purchaser, implies that the substance sold is produced by a process of fermentation. The substance demanded by Mr. Gray was half-a-pint of table vinegar. The substance sold to him was admittedly a synthetic product, and it is not suggested that the seller gave him any information about the substance he sold as table vinegar. It follows that, for the reasons we have given, the article sold to him was not of the nature, quality or substance demanded, and, in our view, in such circumstances was clearly sold to him to his prejudice. The appeal must therefore be dismissed with costs."

The Chairman agreed to state a case if counsel on each side could agree a case together. An order for 75 guineas costs was made.

The Editor is informed that no appeal against this judgment has been lodged, and that the time for appeal has expired.

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

I. HYDROGEN SULPHIDE

THIS is the first of a series of leaflets describing standard methods for the detection of toxic gases in industry.

The Foreword explains that a paragraph of the Chemical Works Regulations, 1922, made under Section 79 of the Factory and Workshop Act, 1901, prohibits entry by any person not properly protected into any place which might contain dangerous gas, until the air has been tested and found safe to breathe. To meet this requirement the question of simple and rapid chemical or other methods for determining low concentrations of dangerous gases, such as may occur in various circumstances in chemical works, was discussed by the Association of British Chemical Manufacturers with the Home Office, and, as a result, arrangements were made by the Department of Scientific and Industrial Research, at the request of the Home Office and with the financial and technical co-operation of the Association of British Chemical Manufacturers, for a series of tests to be developed by the Chemical Defence Research Department.

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* Leaflet No. 1. London: H.M. Stationery Office. June 18th, 1937. Price 3s. 6d. net.

POISONOUS EFFECTS.—In concentrations of 1 in 1000 by vol. or higher, hydrogen sulphide will cause immediate unconsciousness, and will result in death unless artificial respiration is immediately applied. In such concentrations it is nearly as toxic as hydrogen cyanide and may act with equal rapidity by paralysing the respiratory centre of the brain. In weaker concentrations the effects may be summarised as follows:

Concentration in air		Effects
Parts by vol.	Mg. per litre	
1 in 2,000	0·76	Very dangerous if inhaled for 15 to 30 minutes. Causes severe irritation of the eyes and respiratory tract with risk of pneumonia or serious injury to the lungs, which may readily prove fatal.
1 in 5,000	0·304	Dangerous if inhaled for one hour. Causes severe irritation of the eyes and respiratory tract. Eyes are affected after 6 to 8 minutes.
1 in 10,000	0·152	Symptoms of local irritation of eyes and respiratory tract after *one* hour's exposure.

METHODS OF DETECTION.—The lead acetate test has been adopted as a sensitive qualitative test readily adaptable as a quantitative method. Of the various methods of applying the lead acetate test, the only one that was considered satisfactory was that of drawing the atmosphere *through* the test-paper.

It is mentioned that the lead acetate test-paper method has been applied in a continuous automatic detector, in which the stain interferes with a ray of light directed on to a photo-electric cell, and causes a bell to ring (cf. *J. Soc. Chem. Ind.*, **1934**, **53**, 526T).

DETAILS OF THE LEAD ACETATE TEST.—The atmosphere to be tested is sampled by means of a hand exhausting pump with a barrel of approximately 1·25 in. bore and a capacity of 126 ml. To the inlet end of the pump is screwed a spigot with an external screw, 7/16 in. Whit., 14 T.P.I. on 0·437 in. diameter.

Test-papers.—These are made from Whatman No. 1 filter-paper, cut into strips, 2 in. × 4 in. The strips are impregnated with lead acetate solution (10 g. of lead acetate of analytical reagent quality in 100 ml. of water plus 5 ml. of glacial acetic acid), suspended vertically in an atmosphere free from hydrogen sulphide, and left to dry at the ordinary temperature. One inch is then cut off the top and bottom of each strip and discarded. Test-papers can be stored in a glass-stoppered, air-tight container, in which is a drying agent, such as a silica gel capsule. Papers that have been stored more than a fortnight must not be used for the test.

Method.—The lead acetate paper is clamped in a holder of special design (illustrated in the Leaflet), which is screwed into the pump. The apparatus having been tested for leaks by a technique described, a preliminary indication of the atmosphere to be tested is obtained by making two slow and steady strokes of the pump, and the paper is then removed from the holder and compared within 10 minutes with the standard colour chart provided with the Leaflet.* A concentration greater than 1 in 60,000 (0·025 mg. per litre) is thus indicated. If no stain has been produced, further tests are made with fresh lead acetate paper, 3 or 5 strokes of the pump being made and the concentration read off from the chart as before.

The stains obtained should be only on that side of the paper exposed to the gas entering the pump, and the back of the test-paper should remain white (or nearly so if the stain is very heavy).

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* Further copies of the standard stains produced on lead acetate paper can be obtained from H.M. Stationery Office. Price 2s. 1d. post free.

A method is also described for sampling, from a distance, air in a space that is not readily accessible (*e.g.* in acid tanks).

First Aid.—A patient who has been gassed with hydrogen sulphide should be removed into fresh air and wrapped in a blanket to keep him warm. Artificial respiration with oxygen should be started at once and continued even after it may seem to have failed. In one case artificial respiration with oxygen was eventually successful after more than 5 hours.

New Zealand

ANNUAL REPORT OF THE DOMINION ANALYST FOR 1935

The Sixty-ninth Annual Report of the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) summarises the work undertaken for various Government Departments at the main Laboratory in Wellington and the Branch Laboratories in Auckland, Christchurch and Dunedin.

The Reductase Test.—The experience of the laboratory, extending over twenty years, is that the reductase test is the most satisfactory method for controlling the bacteriological purity of milk supplies. The legal standard is at present three hours, but the experience of a number of years shows that this could be raised to five hours.

Zinc in Glazed Earthenware.—Zinc, equivalent to 0·4 g. of the metal per 100 ml. of acid, was dissolved from a sample of glazed ovenware when treated for 30 minutes at cooking temperatures with *N* hydrochloric acid. Zinc oxide is used in glazes to give a matt effect, which was apparent in the sample.

Alkaloid of Ragwort.—An alkaloid with the empirical formula $C_{18}H_{25}O_6N$ was isolated from ragwort (*Senecio jacoboea*) growing in New Zealand. It is probably identical with the alkaloid, jacobine, isolated from Canadian ragwort by Manske. The acetate was very toxic; when injected subcutaneously into rats it produced cirrhosis of the liver.

Fluorescence of Human Hair.—According to a statement in an American journal it is possible to ascertain the race of an individual from the fluorescence of the hair in ultra-violet light. This assertion was investigated in connection with the identification of the body of a half-caste Maori woman. The most suitable arrangement for comparing the fluorescence of hairs was to mount them stretched side by side on a slide made of three-ply veneer stained with aniline black, and to examine them under a microscope in filtered ultra-violet light focused on to the stage by means of a flask, 6 inches in diameter, filled with distilled water; the light was reflected on to the specimens from the silvered inside of a spherical glass basin.

Light hairs fluoresce brightly and grey hair shows a brilliant fluorescence, but in the case under investigation the dark hairs were of particular interest. Specimens of dark brown and black hairs from various races were examined, including European, Chinese, Kaffir, American negro, Syrian, Red Indian, and Maori, as well as half-castes from these races. All the specimens were washed with warm soap solution, rinsed and dried before examination.

The results showed that there was no difference in fluorescence according to race, but that the differences observed simply corresponded with the visual classification of the hair into black and dark brown, black giving a dull blue fluorescence and dark brown a light blue. The method would therefore not be effective for distinguishing hair according to race.

Corrosion of Lead Cable-Sheathing.—The lead-sheathing of a submarine cable at the shore end was found to be extensively damaged by corrosion. Upon removal of the jute wrapping it was seen that very extensive corrosion of the lead had occurred. The corrosion product contained 78·8 per cent. of lead and 13·3 per cent. of carbon dioxide (theoretical for basic lead carbonate 80·1 and 11·4 per cent., respectively). The absence of chlorides, sulphates, nitrates and lead peroxide indicated that the corrosion was not electrolytic, due to stray currents. After removal of the impregnating material from the jute by means of a solvent, the pitch obtained was tested for phenols by azo tests with sulphanilic acid and with *p*-nitroaniline; in each test pronounced positive results were obtained. Confirmation was afforded by Nellensteyn's test with freshly-prepared Millon's reagent (*Proc. World Petroleum Congress*, Vol. II, p. 577). The evidence, therefore, suggested strongly that the corrosion of the sheathing was due to the action of phenols, and was similar to the instances mentioned by the Dutch Corrosion Research Committee on Cables (see *Chem. and Ind.*, 1934, **53**, 565). An interesting sequel to the investigation was that information was sent that the cable concerned was of a new type in which a feature had been made of protecting it against the attack of white ants by impregnation with a preservative compound instead of the customary arsenious oxide; one of the ingredients of this preservative was anthracene oil, and it was from this that the phenols had emanated.

New South Wales

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR 1935

THE Chemical Laboratory of the Health Department is under the control of the Government Analyst (Mr. S. G. Walton). Work is also done for other Government Departments, including the Police Authorities and the Pharmacy Board, and in connection with Coroners' inquiries. Among points of interest in the report are the following:

CHANGE OF FREEZING-POINT STANDARD FOR MILK.—As the result of a survey of genuine samples of milk collected in the milk-producing districts under the Milk Act it was found that occasionally the freezing-point of the mixed milk from a herd of cows gave a figure of —0·535° C. It was considered advisable, therefore, to alter the present freezing-point standard of milk from —0·55° C. to —0·535° C. This does not mean that in the past the vendor has been penalised in any way, for it has been the Departmental practice to allow a tolerance of 3 per cent.

BLEACHED TRIPE.—At the present time the practice of bleaching tripe has become almost general in the Metropolitan area. The treatment consists in (*a*) a preliminary scrubbing and boiling, (*b*) immersion in a peroxide bath, (*c*) washing the bleached tripe, either with or without the addition of acetic acid. To ascertain the effect of bleaching on the tripe, 56 samples of the untreated, and 21 samples of the treated substance were analysed. The following results were obtained:

	Moisture			Alkalinity*		
	Max. Per Cent.	Min. Per Cent.	Average Per Cent.	Max. Per Cent.	Min. Per Cent.	Average Per Cent.
Untreated tripe	92·0	66·3	80·7	0·34	0·013	0·12
Treated tripe	92·6	83·0	89·1	1·17	0·18	0·63

* As Na_2O on the water-free tripe.

The general conclusion arrived at was that the tripe undergoes a pronounced decrease in solid matter and an increase in soluble alkalinity during the process.

The *p*H of 12 samples of untreated tripe ranged from 7·0 to 7·1 and the *p*H of 24 samples of treated tripe from 9·4 to 10·8.

TOMATO PRODUCTS.—With a view to obtaining data for formulating standards for tomato purée and tomato paste, analyses of a number of commercial products were made, with the following results:

	Mould* count Per Cent.	Total solids Per Cent.	Sugars Per Cent.	Ash Per Cent.	Sodium chloride Per Cent.
Concentrated purée ..	22	30·2	13·0	10·2	3·5
Double concentrated conserve	25	44·1	15·5	8·7	0·6
Triple concentrated conserve	50	9·6	3·8	1·3	0·3
Tomato purée	50	10·9	5·1	3·2	0·3
Triple concentrated purée..	50	19·5	7·3	3·4	1·3
Concentrated purée ..	30	16·4	8·1	2·5	0·27
Concentrated purée, 8 to 1	13	35·3	17·1	4·4	0·72
Concentrated purée ..	44	25·3	11·4	4·9	0·35

* The mould count represents the percentage of fields, as determined by the A.O.A.C. official method.

Tomato Pulp.—Regulation 35 (2) of the Pure Food Act (N.S.W.) requires tomato sauce to be prepared from sound and ripe tomatoes. An examination of the mould-content of the proprietary brands of tomato sauce on the Sydney market indicated that a large proportion was made from unsound stock. The mould counts (by the A.O.A.C. official method) of tomato pulps showed that by the use of good stock and efficient sorting no difficulty should be experienced in producing tomato sauce the mould count of which does not exceed 25 per cent. positive. To allow for seasonal conditions, however, it is proposed to introduce a standard imposing a maximum mould count of 50 per cent. of fields positive.

LEAD ARSENATE POISONING.—In a case which formed the subject of a charge of murder a woman administered lead arsenate to her husband in his food. Death did not occur until four or five weeks later. The following results were obtained in the analysis of the exhibits:

Material	Weight of material	Lead found	Arsenic found
Liver ..	3 lb. 14 oz.	5·6 mg.	0·10 mg.
Hair	2·0 g.	—	4·0 mg. per 100 g.
Nails and cuticle	2·0 g.	—	3·0 mg. per 100 g.
Bones ..	800 g.	4 mg. per 100 g.	—

STRYCHNINE POISONING.—In this case the deceased had several fits over a period of about 15 hours. The doctor diagnosed strychnine poisoning, and the patient was removed to hospital for treatment. Death took place in approximately 48 hours after the first fit. From a check of the hypodermic strychnine tablets kept on the premises occupied by the deceased it appeared that the maximum amount of strychnine that could have been taken was 0·4 grain. No trace of strychnine could be found either in the stomach or the organs, and it would seem that in the 48 hours between the taking of the strychnine and death the whole of the alkaloid had been eliminated or destroyed.

POLLUTION OF BEACH SANDS.—An investigation was made to ascertain the extent of pollution of beaches used by the public. The method of determining pollution was as follows:—A sample of the sand was shaken at frequent intervals with an equal amount of distilled water, the sand was allowed to settle, and the supernatant liquid was analysed as in water analysis. From the results obtained it is considered that the organic nitrogen figure for unpolluted beach sands should not exceed 0·02 part per 100,000 of wash water; the figure for slightly polluted sand should not exceed 0·10 part; excessive pollution is indicated if the figure exceeds 0·20 part per 100,000.

DETERMINATION OF ALCOHOL IN HUMAN URINE AND BLOOD.—As the result of various coroners' inquiries it was found necessary to ascertain, from an examination of the urine or blood, the approximate alcoholic condition of persons concerned in accidents. In conjunction with the Medical Officer for Sydney, Dr. A. A. Palmer, an investigation was undertaken into the relationship existing between the amount of alcohol consumed and the amount contained in the urine and in the blood at definite intervals of time after consumption. Different types of alcoholic liquids were used, the subjects selected were of different ages, from 25 to 54 years, and their body weights ranged from 125 to 174 lb. The personal history varied from almost total abstainers to moderate drinkers.

The method of analysis used for urine was a modification of that of Southgate and Carter (*Brit. Med. J.*, 1926, 463), and for the removal of proteins from blood prior to the determination of alcohol the method of Bock was used (*J. Biol. Chem.*, 1931, **93**, 645; Abst., ANALYST, 1932, **57**, 49). In experimental determinations it was found that the loss of alcohol in the process of distillation and determination in urine did not exceed 2 per cent. For the purposes of the investigation known quantities of various alcoholic liquors (wine, beer, whiskey, and rum) were consumed, the wine and beer being taken undiluted, the whiskey diluted with an equal volume of water, and the rum with an equal volume of milk.

From the results of the test experiments the conclusion is drawn that the amount of alcohol found in the urine and blood is a definite indication of the minimum quantity of liquor consumed and the alcoholic condition of the person.

The maximum elimination of alcohol in the urine takes place in 2 to 2½ hours. This opinion was based on the results of averaging the amount of liquor consumed and the time taken in the consumption. The factors given by Evans and Jones (ANALYST, 1929, **54**, 134) for the calculation of the amount of alcoholic liquor consumed from the alcohol-content of the urine at its maximum excretion apply reasonably well for a person weighing about 9 stone. For those weighing approximately 13 stone the factor should be increased in the ratio of 13 to 9. Of the alcohol consumed, approximately 2 to 3 per cent. is eliminated in the urine; apparently, persons of lower body weight eliminate a greater percentage for the same consumption of liquor. It is advisable to collect at least two samples of urine at approximately half-hourly intervals in order to form an opinion as to the minimum amount of alcohol consumed.

British Standards Institution

BRITISH STANDARD METHOD FOR THE DETERMINATION OF VISCOSITY OF LIQUIDS IN ABSOLUTE (C.G.S.) UNITS

This Standard Method (No. 188—1937), revised in May, 1937, has been approved by the Chemical Divisional Council and is published under the authority of the General Council. In earlier editions the term "viscosity" was used to connote "dynamic viscosity," but since the tube viscometers, described in this Standard, give indications of the kinematic viscosity rather than dynamic viscosity, it has become desirable that the results should be normally expressed in terms of kinematic viscosity. This is in agreement with a resolution carried at the World Petroleum Congress in London in 1933.

The Standard is published by the British Standards Institution, 28, Victoria Street, London, S.W.7. Price 2s. net, post free 2s. 2d.

BRITISH STANDARD SPECIFICATION FOR GRADUATED PIPETTES AND STRAIGHT PIPETTES

The series of graduated pipettes (Type 1), calibrated for delivery from the zero mark to the graduation marks, includes the following sizes:

Total	capacity	1 ml.	sub-divided	into	0·01 ml.	intervals
,,	,,	2 ml.	,,	,,	0·02 ml.	,,
,,	,,	5 ml.	,,	,,	0·05 ml.	,,
,,	,,	10 ml.	,,	,,	0·10 ml.	,,
,,	,,	25 ml.	,,	,,	0·10 ml.	,,

Capacity is defined as the volume of water at 20° C., expressed in ml., delivered by the graduated pipette at 20° C., when emptied, in the method specified, from the zero mark to the graduation mark.

British Standard Graduated Pipettes of Type 2, calibrated for delivery down to the jet, must conform with specified dimensions.

The specified method of emptying the pipette leaves a small quantity of water remaining in the jet, and no method of emptying, such as blowing out, which expels liquid completely from the jet, or increases the natural rate of delivery, should be used.

The pipettes in this series have a capacity of 1 ml., 9 ml. and 10 ml., and are calibrated for the delivery of water at 20° C.

Copies of the Specification can be obtained from the Publications Department, British Standards Institution. Price 2s. net, post free 2s. 2d.

BRITISH STANDARD SPECIFICATION FOR DENSITY HYDROMETERS FOR USE IN MILK

This Specification (No. 734—1937) forms part of a series for scientific glassware. One basis of adjustment is adopted for these hydrometers, namely, that they shall indicate density, *i.e.* mass per unit volume, in g. per ml., at 20° C. in a liquid having a surface tension of 46 dynes per cm., instead of the customary practice of using hydrometers for testing milk adjusted to indicate sp.gr., S60° F./60° F. at 60° F. This brings the hydrometers into line with the B.S.I. Specification for Density Hydrometers No. 718—1936 (*cf.* ANALYST, 1937, 129).

Specifications are given for hydrometers of range 1·025 g./ml. to 1·035 g./ml. for use in normal milks, and for hydrometers of range 1·015 g./ml. to 1·025 g./ml. for use in milks of low density.

The following tables to be used in conjunction with hydrometers for use in normal milk are given in an appendix:—(1) Correction for scale errors in hydrometers. (2) Corrections to hydrometer readings to obtain density in g./ml. at the temperature of observation. (3) Corrections to obtain density of milk at 20° C. (4) Table for determination of percentage of total solids and percentage of non-fatty solids. (5) Use of the British Standard Hydrometers in the measurement of milk in bulk.

The Specification may be obtained from the Publication Department, British Standards Institution. Price 3s. 6d. net, post free 3s. 10d.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Colorimetric Determination of Lactic Acid in Milk and Milk Products. F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 130–140.)—The yellow colour produced in the reaction between ferric chloride and lactic acid (Williams, Muller and Neiderl, *Mikrochem.*, 1931, **9**, 268) may be used to determine the latter in milk and milk products. A serum is prepared by the addition of sulphuric and phosphotungstic acids and, although lactalbumin is not completely removed, the small amount present is not sufficient to cause foaming in the liquid extractor, which is of the type previously described (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 435), modified to take 50 ml. of liquid. Part of the citric acid in milk is extracted, but is completely removed by precipitation as barium citrate in an alcoholic medium. The extracted lactic acid is purified with active carbon which, under the controlled conditions, adsorbs only a constant small amount (about 7 per cent.) of the lactic acid present. The carbon used may be Nuchar W, Suchar, Darko G.60 or Carbex E, but not Norit A or animal charcoal, which adsorb greater amounts. Colour comparison may be made in Nessler glasses but, owing to the necessity for treating the standards with active carbon, the process is tedious, and measurement by means of a photometer is more rapid and accurate. The instrument recommended is that described by Clifford and Wichmann (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 130), used with a filter transmitting at about $450 m\mu$. A calibration curve is prepared by treating lithium lactate solutions, containing the equivalent of up to 12 mg. of lactic acid, with active carbon, as described in the process, and plotting the amount of lactic acid present against the photometer readings.

To prepare the standard lithium lactate, heat syrupy lactic acid, diluted with twice its volume of water, nearly to boiling-point, add lithium carbonate gradually until the solution is slightly alkaline to phenol red, re-acidify slightly, evaporate to crystallising point, add five volumes of alcohol and allow the liquid to stand over-night, after which the deposit is re-crystallised from water and dried at 100° C. The active carbon is purified by mixing 10 g. with 30 ml. of N hydrochloric acid and 200 ml. of water and agitating with a current of air on the steam-bath, after which the carbon is filtered off by suction and washed twice with 200-ml. portions of water. The ferric chloride solution used is a 1 per cent. solution in water containing 2·5 per cent. by volume of N hydrochloric acid. To 50 g. of milk (or 5 g. of dried milk with 50 g. of water, or 20 g. of cream or ice-cream made up to 50 ml. with water) add, with constant stirring, 6 ml. of N sulphuric acid, followed by 5 ml. (1 ml. for cream and 2 ml. for ice-cream) of a 20 per cent. phosphotungstic acid solution. Make the mixture up to 100 ml. with water, allow it to stand for several minutes and filter. Pipette 50 ml. of the serum into the inner tube of the extractor, add 0·5 ml. of dilute sulphuric acid (1 + 1) and extract for two hours with 200 ml. of washed ether in which a thread is suspended to ensure even boiling. To the extract add 20 ml. of water and expel the ether on the steam-bath. Neutralise the aqueous residue to phenolphthalein with saturated barium hydroxide solution, make up to about 90 ml. with alcohol, heat almost to boiling, cool, make up to 110 ml. with alcohol and filter. Evaporate 100 ml. of the filtrate to about 10 ml., add about 50 ml. of water and again evaporate to 10 ml. From a burette add 3·3 ml. of $N/10$ hydrochloric acid, make up with water to about 40 ml., add 200 mg. of active carbon and heat on the steam-bath for 10 minutes. After cooling the liquid, make up to 55 ml. and filter, pouring back until a bright filtrate is obtained. Transfer 10 ml. of the filtrate to a Nessler glass, add sufficient $N/10$ hydrochloric acid to bring the amount present to 3 ml., and make the mixture up to about 40 ml. with water. Place the Nessler glass in a jacket of black paper and add, from a burette, 5 ml. of ferric chloride solution, make up to 50 ml. with water and mix. Dilution is not permissible after the colour has developed. Fill a 4-in. cell, the walls of which have been painted black, with the solution, and read in the photometer. Determine the amount of lactic acid in the 10-ml. portion from the calibration curve and, if necessary, repeat the determination with an amount of solution which will not overstep the 12 mg. limit of lactic acid. If a photometer is not available, place 5 ml. of standard lithium lactate solution (1 ml. = 1 mg. of lactic acid) in a Nessler glass, add 3 ml. of $N/10$ hydrochloric acid, make up to about 40 ml. with water, wrap the glass in black paper, add 5 ml. of ferric chloride solution, dilute to 50 ml., and compare the colour with that of the 10-ml. portion of filtrate prepared as described above. If the colours do not match, repeat with a suitable amount of the standard solution. Having thus ascertained the approximate amount of lactic acid present, transfer a portion of the remaining filtrate, containing not more than 10 mg. of lactic acid, to a Nessler glass and produce the colour as described. Prepare a suitable series of standards, subjecting these to the active carbon treatment as described in the process.

To calculate the amount of lactic acid in the original sample, an allowance must be made for the volume of insoluble solids. For this purpose the sp.gr. of butter-fat is taken as 0·9 and that of casein as 1·3. If S is the volume of insoluble solids, A the aliquot portion taken for the final determination, and W the weight of the sample, the amount of material in the final aliquot part is

$$\frac{W}{100-S} \times \frac{50}{110} \times \frac{100}{55} \times A.$$

For butter, the general method is the same, but it is necessary to remove the fat. A 20-g. portion of butter is warmed on the steam-bath with 15 ml. of water and 0·5 ml. of N sulphuric acid. The liquid is then neutralised with $N/10$ sodium hydroxide solution, and transferred with 15 ml. of water to a centrifuge tube. Ether (50 ml.) is added, the tube is gently shaken, and an equal amount of petroleum spirit is added. After centrifuging, the ethereal layer is removed by means of a siphon with a turned-up end, and the extraction is repeated with 25-ml. portions of the solvents. The aqueous layer is acidified with 3 ml. of N sulphuric acid, warmed to expel ether, cooled and treated, drop by drop, with phosphotungstic acid solution. The mixture is made up to 100 ml. and filtered, and 50 ml. of the filtrate are transferred to the extractor. By this method the determination of 10 parts of lactic acid per million is possible. A. O. J.

Colorimetric Determination of Lactic Acid in Tomato Products. F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 303–307.)—Bacon and Durbar (*U.S. Bur. Chem.*, Cir. 78) found that sound tomatoes contain little or no lactic acid, but that formation of this acid is associated in some instances with their spoilage. It may be determined by a modification of the author's method for the determination of lactic acid in milk (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 130; see preceding abstract). A 20-g. portion of tomato paste, catsup or chili sauce or a 40-g. portion of tomato juice is made up to 200 ml. with water and filtered. If filtration is slow, the liquid may be centrifuged and subsequently filtered with the aid of kieselguhr (Filtercel). A 50-ml. portion of the filtrate is transferred to a liquid extractor of the type previously described (*J. Assoc. Agr. Chem.*, 1933, **16**, 435) modified to take 50 ml., 1 ml. of dilute sulphuric acid (1 + 1) is added, and extraction with ether is continued for 3 hours. With catsup and other products containing acetic acid the extract, after removal of the ether, is made up to 50 ml. and distilled in steam until 250 ml. of distillate have been collected. The residue is then free from acetic acid. The extract after removal of the solvent is dissolved in 20 ml. of water, neutralised to phenolphthalein with saturated barium hydroxide solution, transferred to a 110-ml. flask with alcohol, and made up to the volume with alcohol, and 100 ml. are filtered. The procedure is then exactly as described (*loc. cit.*) with the exception that a filter transmitting at $460 m\mu$ is used in the photometer. To test the accuracy of the method, varying amounts ranging from 1 to 75 mg. of lactic acid as lithium lactate were added to tomato juices of good quality. By this method 93 to 99·9 per cent. of the lactic acid added was found. For catsup and other products containing acetic acid and necessitating steam distillation, the lactic acid found was 93·6 to 98·7 per cent. of that added. The lactic acid found in 13 samples of authentic tomato juice varied from 3·3 to 8·0 mg. per 100 g. In six samples of commercial catsup 23·6 to 28·4 mg. per 100 g. were found. Two samples of tomato paste gave 19·8 to 25·4, one sample of pulp 5·5, and two samples of chili sauce 21·2 and 27·2 mg. per 100 g. In the results quoted in the paper the small amounts of lactic acid, found in samples to which none had been added, are interpreted as material reacting as lactic acid under the conditions of the method of analysis. A. O. J.

Chemical Composition of Avocado Fruits. A. R. C. Haas. (*J. Agric. Res.*, 1937, **54**, 669–687.)—The acidity and contents of fat, sugar, and minerals in different parts of avocado fruits were determined. The acidity of the pulp decreases from *p*H 6·44 in the outer portion of the tip to *p*H 6·86 in the inner portion of the stem-half of the fruit. The fat showed no local accumulation and varied in fruits of different varieties and ages from 1·73 per cent. of the fresh weight to 28·87 per cent.; the fat-content increases with increasing maturity. The total and reducing sugar-contents of the stem-halves (0·65 to 2·05 per cent. of the fresh weight and 0·54 to 1·48 per cent., respectively) were slightly higher than those of the tip-halves (0·52 to 1·74 per cent. and 0·29 to 0·84 per cent., respectively) in unripe fruits and decreased with increasing maturity, the difference between the contents of tip- and stem-halves also decreasing with ripening. The percentage of dry matter on the fresh weight is usually higher in the tip-halves than in the stem-halves, some figures for fruits of different varieties being 21·34, 12·37, 12·81, and 14·12 per cent. in the tip-halves, as compared with 20·74, 11·73, 12·03, and 13·24 per cent. in the stem-halves; the dry matter increases with increasing maturity. The ash (3·40 to 4·75 per cent. on the dry substance) is higher in the tip-halves than in the stem-halves. Potassium is the most abundant constituent of the ash. The percentages of potassium, manganese, copper, and nitrogen (including nitrates) are higher in the tip- than in the stem-halves, calcium, total sulphur and total chlorine being more abundant in the stem-halves. Sodium and iron are present but show no local accumulation. The content of sodium increases and the contents of inorganic phosphate and manganese decrease with increasing maturity. E. M. P.

Sugar as an Inhibitor of Corrosion in Canning. H. C. S. de Whalley. (*Chem. and Ind.*, 1937, **56**, 569–570.)—The Food Investigation Special Reports Nos. 40 (ANALYST, 1931, **56**, 315), and 44 (ANALYST, 1936, **61**, 193) of the Department of Scientific and Industrial Research showed that crude beet and cane sugars have greater inhibiting effects on the corrosion of iron than have the refined sugars, the effect being greater with raw beet sugar than with raw cane sugar. Inhibiting effects of different samples of some kinds of sugar varied considerably, which suggests that the inhibiting substances are breakdown products or other impurities. Refined sugars with inhibiting action usually gave pale yellow solutions. Treatment with alumina cream or decolorising carbons lessened inhibiting action; extraction of raw beet sugar with alcohol gave a dark brown sticky mass with a powerful inhibiting effect. The following are analyses of some raw beet sugars of good grade:

	1	2	3	4	5
Polarisation	98·00	98·40	98·67	98·25	98·05
Invert sugar, per cent. ..	—	—	—	—	—
Ash, per cent.	0·36	0·27	0·29	0·41	0·37
Moisture, per cent.	0·95	0·79	0·72	0·85	0·88
Undetermined	0·69	0·54	0·32	0·49	0·70

Refined white sugar (Pure Gran from Tate & Lyle carton) gave the following results: Polarisation (or sucrose), 99·956; invert sugar, 0·006; ash, 0·006; water, 0·020; organic matter, 0·012.

The ash and undetermined substances in the raw beet sugars would include the inhibitor. Spectrographic analysis of the same sugars indicated the following amounts of metals in parts per million:

	Raw beet sugars					Refined white sugar
	1	2	3	4	5	
Copper	4·0	3·6	4·2	5·9	4·1	0·1
Lead	3·2	2·4	3·2	4·5	0·4	0·1
Manganese ..	4·0	3·0	3·2	4·5	4·1	0·05

The inhibitive effect may be due to the presence of these traces of metals, which would be picked up by the sugar juices and liquors in contact with metallic apparatus. E. M. P.

Physical and Chemical Properties of Casein Fat. S. G. Stevenson and A. L. Bacharach. (*Biochem. J.*, 1937, **31**, 721–723.)—The fat in lactic-acid casein is between 1·0 and 2·5 per cent., and it may be extracted with hot 95 per cent. alcohol. The ethereal extract of the residue obtained by evaporating the alcoholic extract of a New Zealand casein was a yellow fat, which was examined in order to ascertain if hydroxystearic anhydride previously reported by Kon and Funk (*Biochem. J.*, 1924, **18**, 1238) was present. This compound was not found, and the results obtained indicated a slightly modified butter-fat. Although the gross difference between this fat and butter-fat was not great, it was found that the total unsaponifiable matter had increased threefold, and that the liquid portion had been even more concentrated than the sterol fraction. S. G. S.

Fatty Acids Associated with Banana Starch. L. Lehrman and E. A. Kabat. (*J. Amer. Chem. Soc.*, 1937, **59**, 1050–1051.)—Dried pulp from green bananas could not be used directly for the estimation, since some naturally occurring substance made the dried residue after hydrolysis difficult to pulverise. Banana starch was therefore isolated, and to make sure that any fatty acids found were not present extraneously, the starch was extracted with alcohol before use. The aqueous filtrate from the hydrolysis was tested for glycerol, and the result proved that glycerides were not the source of the fatty material. The amount of fatty acids liberated by hydrolysis of banana starch was then found to be 0·2 per cent. and consisted of a light yellow semi-solid with iodine value 59·4. The acids were a mixture of palmitic, oleic, linolic and linolenic, with a very small amount of phytosterol, this being the first time that phytosterol has been found combined in a starch. The bromination method was found more effective than oxidation for the detection of the small amounts of linolenic acid in the presence of oleic and linolic acids. D. G. H.

Seeds of *Cichorium intybus*, Linn. R. N. Mistra and S. Dutt. (*J. Indian Chem. Soc.*, 1937, **14**, 141–143.)—*Cichorium intybus* (chicory or Kasni in Hindustani) Nat. Order, *Compositae*, is found in north-west India and its seeds, reputed to be tonic, demulcent and cooling, are used in Indian medicine. The plant is prescribed very much as *Taraxacum* (dandelion) is in Europe. The seeds examined contained oil 4·7 per cent.; phlobaphenes 1·0; and tannin 1·0; also reducing sugars. They yielded 13·8 per cent. of ash (17·5 per cent. soluble and 82·5 per cent. insoluble in water), consisting mainly of potassium, sodium (traces), calcium, aluminium, sulphate, phosphate, chloride, carbonate and silica. The oil, as extracted with benzene, had the consistence of honey and gave the following analytical figures:—Sp.gr. at 22° C. 0·9229; n^{30}, 1·3795; solidifying pt., − 11° C.; saponification value, 193·1; iodine value, 95·6; acetyl value, 14·8; Hehner value, 93·9; unsaponifiable matter, 1·7 per cent. The fatty acids melted at 35 to 38° C. and had sp.gr. at 40° C. 0·8931; neutralisation value, 192·5; mean molecular wt. 291·4; iodine value, 104·8. They consisted of 21·7 per cent. of saturated and 78·3 per cent. of unsaturated acids. The unsaturated acids consisted of 42·8 per cent. of oleic and 57·2 per cent. of linolic acid, and the saturated acids after esterification and fractional distillation were shown to consist of palmitic and stearic acids. The unsaponifiable matter contained sterol. D. G. H.

Philippine Curcas Nut Oil. A. O. Cruz and A. P. West. (*Philippine J. Sc.*, 1936, **61**, 437–444.)—The Curcas or Physic nut is the seed of the small tropical American tree, *Jatropha curcas*, which is grown in other countries, including the Philippine Islands, as a hedge plant. The seeds are enclosed in rounded capsules. The general characters of the oil have been determined by various investigators, but data on the composition of the oil are meagre and contradictory. The present sample, collected from the Pampanga Province, Luzon, consisted of 34·3 per cent. of hulls and 65·7 per cent. of kernels. The kernels had a moisture-content of 20 per cent., and the yield of oil on extraction with ether was 38·2 per cent. of the dry seeds. After the crushed kernels had been cold pressed the resulting oil cake (which cannot be used as a cattle food owing to the presence of a toxic purgative substance) consisted of:—Moisture, 6·63; oil, 14·4; protein, 49·90; crude fibre, 3·45; ash, 8·87; carbohydrate (by diff.), 17·01 per cent. The fertiliser constituents in the cake were nitrogen, 8·23; phosphoric anhydride, 4·71; potash, 0·25 (moisture, 8·05 per cent.). The oil had the following characteristics:—Sp.gr. at 30°/4° C., 0·9082; n^{30}_{D}, 1·4665; saponification value, 192·4; iodine value (Hanus), 94·8; acid value, 5·1; unsaponifiable matter, 0·45 per cent.; saturated acids (corr.), 16·82 and unsaturated acids (corr.), 78·00 per cent., the latter of iodine value, 111·0. The unsaturated acids consisted of linolic acid, 22·9, and oleic acid, 77·1 per cent. The saturated acids, the proportions of which were calculated from data of analyses of the fractions obtained by distilling the methyl esters, were myristic, 2·56; palmitic, 67·14; stearic, 28·81; arachidic acid, 1·49 per cent. The percentage composition of the whole oil (as glycerides of the acids) was: oleic, 62·86; linolic, 18·65; myristic, 0·45; palmitic, 11·84; stearic, 0·26; arachidic, 0·26 per cent. D. G. H.

Philippine Tobacco Seed Oil. A. O. Cruz and A. P. West. (*Philippine J. Sci.*, 1936, **61**, 161–168.)—The tobacco seeds examined were a mixture of the Vizcaya and Espada varieties from plants grown in the Cabagan and Cagayan districts. The ground seeds were extracted with ether and the oil, after treatment with kieselguhr, Suchar and talcum powder, was of a light yellow colour. The yield was 39·92 per cent. of the dry seeds and the analytical figures were:—Sp.gr. at 30/4° C., 0·9130; n^{30}_{D}, 1·4714; saponification value, 190·5; iodine value (Hanus), 135·8; acid value, 16·8; unsaponifiable matter, 1·41 per cent. The saturated acids were (corr.) 9·99 and the unsaturated acids (corr.) 82·87 per cent. of the total fatty acids; the iodine value of the unsaturated acids was 153·6. The fatty acids were separated by the lead salt and ether method. Analyses of the fractions obtained by distillation of the methyl esters from the saturated acids showed the acids to consist of myristic, 0·49; palmitic, 67·08; stearic, 29·10; arachidic, 3·33 per cent. The unsaturated acids consisted of 69·55 per cent. of linolic and 30·45 per cent. of oleic acid. The oil is thus a semi-drying oil similar to kapok and cottonseed oils and appears to be suitable for the same purposes.

D. G. H.

Green Turtle Oil. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 185–186B.)—A specimen of green turtle oil from *Chelonia japonica*, Thunberg, from the Bonin islands, consisted of a mixture of body and liver oils, and was an orange-yellow liquid, showing a deposit at ordinary temperature. Very little colour was given with the antimony trichloride test, and in the Tortelli–Jaffé test an orange-yellow colour developed without green fluorescence. The analytical figures for the oil were as follows, and agreed with those obtained by Lee for African turtle oil (ANALYST, 1935, **60**, 650): sp.gr. at 20°/4° C., 0·9150; n_D^{20}, 1·4662; saponification value, 205·8; iodine value (Wijs), 64·1; acid value, 1·36; unsaponifiable matter, 0·52 per cent. The fatty acids melted at 28–29° C. and had neutralisation value 211·4 and iodine value 65·8. The ether-insoluble (5.0 per cent.) and petroleum spirit-insoluble (7·6 per cent.) bromides were isolated and the proportion of bromine present determined. The fatty acids were converted into their methyl esters and fractionally distilled, and the fractions were examined for their component acids. The chief constituent was oleic acid, and myristic, palmitic and stearic acids were also present, with a small proportion of the highly unsaturated acids C_{20} and probably C_{18}. The proportion of myristic acid was fairly large and lauric and possibly zoomaric (palmitoleic) acids were present. Dodecenoic and tetradecenoic acids were not identified with certainty. The oil differs from most marine animal oils in the comparative lack of C_{20} and C_{22} acids. The presence of cholesterol in the unsaponifiable matter was confirmed. D. G. H.

Observations on the Chemical Determination of Adrenaline. J. Devine. (*Biochem. J.*, 1937, **31**, 545–550.)—The variations in the estimation of adrenaline by the Folin method have been found to be due to the ascorbic acid present and to the *p*H at which the colour is developed. The ascorbic acid causes high values to be obtained, and an incorrect *p*H value may cause low values to be recorded. These sources of error may cancel one another, so that a determination may be in good agreement with the pressor assay. If the amount of ascorbic acid is determined and the Folin value corrected for this, the results agree well with those obtained in iodine determination of adrenaline and also with the pressor assay. The previously observed, but unidentified catechol compound, which is also present in the suprarenal gland, does not give a colour on oxidation, has little or no pressor activity, and does not affect the Folin reagent. Apart from this compound, the claim that an adrenaline precursor exists in the gland is not confirmed.
S. G. S.

Hydnocarpic and Chaulmoogric Acids and Ethyl Esters. H. I. Cole and H. Cardoso. (*J. Amer. Chem. Soc.*, 1937, **59**, 963–965.)—Pure chaulmoogric acid may best be prepared from the oil of *Oncoba echinata* or *Hydnocarpus alcalae*, for these oils do not contain hydnocarpic acid, but since no oil is known that contains hydnocarpic but not chaulmoogric acid, to prepare hydnocarpic acid it must be separated from chaulmoogric acid. This may be done successfully by employing a combination of fractional vacuum distillation of the ethyl esters in a high-temperature fractionating apparatus, and fractional crystallisation of the free fatty acids separated from the esters. The free fatty acids from *Hydnocarpus Wightiana* oil were obtained, washed in hot water, solidified, re-melted, esterified with 99 per cent. ethyl alcohol and, after standing overnight, treated with an equal volume of water. The ester was extracted with ethyl ether and washed, and free acids were removed with a 10 per cent. solution of sodium carbonate. The ethereal solution was washed with water, dried with calcium chloride, filtered and evaporated. The ethyl esters were distilled at 10 mm. pressure; one fractionation separated the ethyl hydnocarpate from the chaulmoograte, though not from the other solid and liquid acids. The fractions were separated and, after dilution with hot water, an excess of 15 per cent. sulphuric acid was added; the liberated fatty acids were washed four times with hot water, and crystallised to constant m.p. and optical rotation from 80 per cent. alcohol. The specific rotation of the crystals was found to be a more sensitive indication of purity than the m.p. Crystals of pure hydnocarpic and of pure chaulmoogric acids grow upward in branching forms from the melted acids as they solidify, and even a small proportion of impurity inhibits this growth, yielding instead a flat surface. Further re-distillation of the esters of the acids and crystallisation caused no change in the constants.

	Hydnocarpic acid	Chaulmoogric acid	Ethyl hydnocarpate	Ethyl chaulmoograte
M.p. °C.	60·5	68·5	—	—
B.p. °C. (10 mm.)	—	—	184	206
$[\alpha]^{25}_{D}$	69·3	60·3	61·94	55·42
Sp.gr. 20°/4° C.	—	—	0·911	0·904
25°/4° C.	—	—	0·907	0·901
30°/4° C.	—	—	0·904	0·898
n_D 20°	—	—	1·4597	1·4610
25°	—	—	1·4578	1·4592
30°	—	—	1·4558	1·4573
Iodine value (Hanus) ..	100·7	90·5	—	—
Neutralisation equivalent	251·8	280·9	—	—

Even a small percentage of palmitic acid lowered the m.p. of hydnocarpic acid to a surprising degree; the m.p. curve is given. Mixtures of the two pure acids (chaulmoogric and hydnocarpic) were made up and the m.p. curve was plotted; the mixture of lowest m.p. was not at the point of a molecular mixture, but the mixtures of the acids showed a very sharp drop in m.p. and a loss of the characteristic crystalline forms of the pure acids. The very high specific optical rotation makes this value a particularly useful means of determining the purity of the acids, and if an electric sodium lamp is used in conjunction with a precision polarimeter different observers can agree with each other to within ± 0·02°. Recorded values for $[\alpha]_D$ of chaulmoogric acid are often too high on account of admixture with a small proportion of the more optically active hydnocarpic acid.

D. G. H.

New Colour Reaction for Morphine and its Derived Alkaloids. M. Pesez. (*J. Pharm. Chim.*, **1937**, **25**, 504–508.)—The reactions of Froehde, Mandelin, Erdmann and Denigès and other reactions commonly used for the identification of morphine have the disadvantages that they are not absolutely specific for morphine and that they do not yield permanent colours. The following reaction, depending upon the action of nascent bromine, is free from these disadvantages. Morphine or one of its salts (0·1 to 0·2 g., or 3 or 4 drops of an aqueous solution) is added to 2 ml. of conc. sulphuric acid in a test-tube, and the mixture is shaken until the solid matter is dissolved. Two drops (0·1 ml.) of a 10 per cent. potassium bromide solution are added, and the test-tube is placed in a boiling water-bath for 3 minutes. The yellow colour (due to free bromine) changes to yellowish-brown and finally to deep yellowish-green. When cold, the mixture is carefully diluted to about 20 ml. with water. A fine emerald-green colour is formed with 0·1 g. of morphine, and a paler green with smaller amounts. The colour is due to a green water-insoluble compound, which ultimately separates as a green precipitate, the separation being accelerated by boiling. The coloured substance is soluble in the following solvents, forming coloured solutions:—Xylene (blue), chloroform (bluish-green), ether (pale blue), benzene and ethyl acetate (violet-blue) and in methyl and ethyl alcohols and acetone (greenish-blue). It may be extracted by any of the above-mentioned solvents that are immiscible with water. By re-crystallisation from alcohol, fine needle-shaped crystals or stellate groups of needles are obtained. From its solution in acetone the compound separates as an amorphous powder. The bluish-green solution in chloroform exhibits a wide absorption band in the orange-yellow region of the spectrum. Saturated bromine water may be used instead of potassium bromide, but the reaction is not given when solutions of chloride, iodide, bromate or hypochlorite are used. Codeine, dionine and heroin give the reaction. Thebaine dissolves in cold sulphuric acid, giving an orange solution which, on the addition of potassium bromide and heating on the water-bath, changes to yellowish-brown and, on dilution, to a fine green. The solution obtained by extraction with chloroform is slightly different from that obtained with morphine, its colour being nearer blue. Narcotine gives a red colour before dilution, but the colour disappears on the addition of water. Narceine gives a golden-yellow solution changing to pale yellow and finally to orange-red, and this disappears on dilution. Apomorphine gives a solution of wine colour intensified by heating on the water-bath, but disappearing on dilution. Papaverine gives only the yellow colour of free bromine. The other alkaloids with an oxyphenanthrene structure, such as colchicine and hydrastine, do not answer to the test. Other alkaloids and glucosides which have been tested give colours ranging from yellow to brown before dilution and either colourless solutions or white precipitates on dilution. The reaction is given by the mixed alkaloids of opium (pantopon, etc.). Scopolamine, which gives a negative reaction and sometimes occurs with morphine in preparations for injection, does not interfere with the test. The reaction is affected by the presence of some compounds, and it is usually necessary to separate morphine by extraction with chloroform from a solution rendered alkaline by ammonia. The possibility of the adaptation of the reaction to the quantitative determination of opium and morphine is being investigated. A. O. J.

Lipids of "Russian" Cantharides (*Lytta vesicatoria* Fb.). M. M. Janot and P. Faudemay. (*Bull. Soc. Chim.*, 1937, **4**, 1149–1151.)—The constitution of the lipids of cantharides has scarcely been studied since Gossman's results (*Ann. Chem. Pharm.*, 1853, **86**, 317–330; 1853, **89**, 123–125) were published. Preliminary tests on five samples of *Lytta vesicatoria* of different origin, gave the following results:

No.	Origin	Moisture Per Cent.	Ash Per Cent.	Lipids Per Cent.	Cantharidin Per Cent.
1	Russia	6·8	6·5	13·5	0·70
2	Russia	6·4	9·9	3·5	0·46
3	Russia	9·3	9	4·2	0·40
4	Spain	9·3	5·5	12·7	0·45
5	Roumania	8·8	7	9·3	0·45

The lipids were extracted with petroleum spirit of b.p. 30–50° C. For a full analysis, for which only samples 1 and 2 were available in sufficient quantity, petroleum spirit of b.p. 50–70° C. was used. The residual fat was then extracted with ether. The fats from both samples consisted of free palmitic, stearic, oleic, linolic, and linolenic acids, their glycerides, and compounds of these acids with sterols. In the unsaponifiable matter the following were detected:—Cholesterol, a second sterol which was not identified, and two hydrocarbons, one of which was heneicosane $C_{21}H_{44}$. While Nos. 1 and 2 were qualitatively identical, quantitatively they differed greatly. In No. 1, the composition of the ethereal extract after separation of chlorophyll and cantharidin was practically the same as that of the petroleum spirit extract, and results for the whole derivatives, expressed as free fatty acids, were:—Palmitic, 37; stearic, 4; oleic, 32; linolic, 6, and linolenic acid, 3 per cent.; unsaponifiable matter, 10; undetermined, 8 per cent. The free acids form 65 per cent. of the total fatty matter. No. 2 gave the following results for the two extracts:—

Petroleum spirit extract	Per Cent.	Ethereal extract	Per Cent.
Saturated acids..	36	Saturated acids ..	19
Unsaturated acids	29	Unsaturated acids ..	44
Unsaponifiable and neutral products of saponification..	32	Unsaponifiable ..	16
		Chlorophyll	12
Undetermined	3	Undetermined ..	9

These important quantitative variations indicate that this beetle cannot be classified physiologically by the fat constants or the percentage of lipids. Some of the methods of separation are described and the constants of the different constituents are given.

E. B. D.

Biochemical

Chemical Composition of Teeth. V. Spectrographic Analysis. F. Lowater and M. M. Murray. (*Biochem. J.*, 1937, **31**, 837–841.)—Spectrographic examination, particularly for "trace elements," has been made of human enamel and dentine, dog dentine and rats' teeth, over the range 210$m\mu$ to 620$m\mu$. Special consideration was given to the identification of fluorine, and the specimens analysed included "mottled teeth" from Maldon, Essex, and teeth from rats fed on a fluorine-containing diet. In addition to the major constituents known to be present in dental tissues, the following elements were found in all samples: sodium, silver, lead, strontium, barium, chromium, tin, zinc, manganese, titanium, nickel, vanadium, aluminium, silicon, boron, copper and iron. Teeth of normal dogs and rats do not contain fluorine, but in human teeth from London there was a "possible trace"; there was a definite trace in the human "mottled teeth" and a considerable amount in the fluoride-fed rats' teeth. Potassium was present in the enamel and dentine of "mottled teeth" and in the teeth of rats fed on a diet containing fluorine, but was not found generally. The teeth of fluoride-fed rats contain less iron than those of the normal animal. S. G. S.

Quantitative Method for the Isolation of *l*-Cystine from Keratin (Horsehair). A. Weidinger. (*Rec. Trav. Chim. Pays Bas*, 1937, **56**, 562–564.)—The fat-free sample is heated for 8 hours on a sand-bath under a reflux condenser with a 4-fold volume of 20 per cent. hydrochloric acid, and most of the acid is then removed under reduced pressure at 60° C. A sufficient quantity of sodium acetate crystals is added to the warm solution to bring the *p*H to about 4·0, bromophenol blue being used as indicator, and after 4 days the resulting precipitate is separated by filtration and dissolved in 4 per cent. hydrochloric acid. This solution is decolorised with phosphate-free animal charcoal, which should previously have been boiled with 25 per cent. hydrochloric acid and washed well. The cystine adsorbed on the charcoal is extracted by boiling the mass three times with 4 per cent. hydrochloric acid. The extracts are filtered and evaporated to a small volume on the water-bath under reduced pressure, after which a warm 100 per cent. solution of sodium acetate and an equal volume of acetone are added. After 2 days at room temperature the precipitated cystine is collected in a weighed Gooch crucible, washed with cold water, dried at 95° C. and weighed. The important features of the method are:—(1) The period of initial hydrolysis, which is adjusted so as to obtain complete hydrolysis of the cystine without racemisation. (2) The complete removal of cystine from the activated carbon by heating it three times with acid. (3) The adjustment to the correct *p*H for precipitation. (4) The use of reduced pressure during evaporation to avoid decomposition of the cystine. (5) The use of acetone as an aid to precipitation. Horsehair was found to contain 12·5 per cent. of cystine ($[\alpha]_D$ − 206°; sulphur-content, 26·5 per cent.) as compared with the maximum value of 8 per cent. found by previous methods. Since the sulphur-contents calculated from the cystine-content and found in the horsehair were 3·32 and 3·45 per cent., respectively, the isolation of the cystine must have been almost complete. It has been stated recently that up to 5 per cent. of methionine occurs in wool and in the skin of cattle, but the above-mentioned results and the fact that the filtrate after hydrolysis is free from sulphur, indicate that this substance is not present in horsehair. J. G.

Fat Metabolism in Fishes. XI. Specific Peculiarities in Depot Fat Composition. J. A. Lovern. (*Biochem. J.*, 1937, **31**, 755–763.)—Specific peculiarities in the composition of fatty acids from the fats of certain species and families of fish have been reported from time to time. It has also been shown that the fats from fresh-water fish form a type distinct from those of marine fish. This difference is found to be due to the fat ingested by the species. In certain fish the degree of average unsaturation of one or more of the acid groups may be characteristically abnormal. In *elasmobranch* fish, for example, certain acids may be either unusually saturated or unusually unsaturated, and it is suggested that both types of peculiarity may be due to the appropriate modification of a reversible hydrogenation—dehydrogenation enzymic system. In some instances the acids of the relatively saturated type are accompanied by chimyl, batyl and selachyl alcohols, and it is further suggested that these have been produced by different modifications of the hydrogenation system. The unsaturation aspect of the peculiarities is shown by halibut and turbot. Certain fish show a regular abnormality in the proportions of their various fatty acids. Acids having a lower molecular weight are either reduced or increased, with a corresponding increase or reduction of the higher acids. Instances of this type are certain *elasmobranch* fish, halibut and turbot. The molecular size may control this type of irregularity. Other fish may exhibit peculiarities of an irregular nature, the content of a certain acid or acids being increased or decreased without reference to other acids. Ratfish and catfish have a high content of C_{18} acids and in the tunny C_{14} acids are virtually absent. A compromise may occur when the two opposing sets of requirements are found in the same fish. In the brown trout, for instance, the characteristics of the *Salmonidae* family clash with the fresh-water habitat of the fish, and in the lampern, sea-feeding and fresh-water feeding by the same animal to some extent neutralise one another in their effect on the fat. S. G. S.

Bromine Value of Urines. M. B. Drevon and J. Hagopian. (*J. Pharm. Chim.*, 1937, **25**, 244–254.)—The bromine value of urine, first proposed by Bezssonoff, Vallette and Sacrez (*Bull. Soc. Chim.*, 1935, **17**, 1573) as an indication of a normal physiological condition, has been the subject of a critical investigation by the present authors. In a carefully controlled experiment the volume of urine excreted, the density, the bromine value, the dry residue, the total nitrogen, the nitrogen by formol titration and the ratio of the bromine value to the residue were determined, but no significant relationship was found. For a normal man, for a man after vaccination with typhoid-paratyphoid vaccine, for a normal guinea-pig and for a guinea-pig poisoned with benzene or dinitrophenol, the variation in the bromine value was comparable with that of the density or the dry residue. The authors therefore conclude that the bromine value has no apparent physiological significance. S. G. S.

Carotene of Milk-fat. A. E. Gillam and M. S. El Ridi. (*Biochem. J.*, 1937, **31**, 251–253.)—Early experiments on the chromatograph adsorption of carotene from milk-fat indicated that α- as well as β-carotene might be present. More recent work has shown that with repeated adsorption β-carotene changes into an α-carotene-like compound (*pseudo*-α-carotene). In the present investigation purified carotene from a mixed sample of colostrum and ordinary milk-fat has been found by analyses, melting-point, absorption spectra and optical rotation to be practically pure β-carotene. α-Carotene was either absent altogether, or was present in amounts less than 0·3 per cent. of the total carotene. S. G. S.

Ascorbic Acid Content of a Number of Citrus Fruits. E. P. Daniel and M. B. Rutherford. (*J. Agric. Res.*, 1937, **54**, 689–693.)—Ascorbic acid values were determined by the method of Bessey and King (*J. Biol. Chem.*, 1933, **103**, 687–698; Abst., ANALYST, 1934, **59**, 122) on the following freshly picked citrus fruits: 8 varieties of oranges, 3 of grape-fruit, 2 of tangerines, 8 of tangelos (grape-fruit-tangerine hybrid), and one each of tangor (tangerine-orange hybrid), lemon, lime, limequat (lime-kumquat hybrid), orangequat (tangerine-kumquat hybrid), and Perrine lemon (lemon-lime hybrid). The results obtained were as follows:

	Ascorbic acid content of juice, mg. per ml.
Orange (*Citrus sinensis*)	0·32–0·62
Grape-fruit (*C. grandis*)	0·64, 0·33–0·38
Tangerine (*C. nobilis deliciosa*)	0·18–0·37
Tangelo (*C. nobilis deliciosa* × *C. grandis*)	0·18–0·64
Tangor (*C. nobilis* × *C. sinensis*)	0·40
Lemon (*C. limonia*)	0·33
Lime (*C. aurantifolia*)	0·22
Limequat (*C. aurantifolia* × *Fortunella japonica*)	0·17
Orangequat (*C. nobilis* × *F. japonica*)	0·23
Perrine lemon (*C. aurantifolia* × *C. limonia*)—	
Fresh picked	0·40
Picked in ripe-yellow stage and stored in cold storage Oct. 23—Dec. 19	0·24
Picked in light-green stage and stored in cold storage Oct. 23—Dec. 19	0·26

E. M. P.

Ascorbic Acid Oxidase. W. Stone. (*Biochem. J.*, 1937, **31**, 508–511.)—A number of vegetables and fruits have been examined for (*a*) their ascorbic acid content by extraction with 10 per cent. metaphosphoric acid, (*b*) the ascorbic acid of their expressed juices, before and after treatment with hydrogen sulphide, (*c*) the activity of the expressed juices in oxidising the ascorbic acid of orange juice, with a view to determining which, if any, contained an ascorbic acid oxidase. The vegetables which lost their indophenol-reducing power on mincing (banana, cabbage, carrots, cucumber, potato, string beans and vegetable marrow) were able to oxidise the ascorbic acid of orange juice, thus showing an ascorbic acid oxidase to be present. Those which retained their ascorbic acid content (cantaloupe melon, green peas, lettuce, lucerne, onions, spinach, and water melon) had no effect on orange juice and hence had no oxidase. The enzyme catalysed the reversible oxidation of ascorbic acid to dehydro-ascorbic acid, a recovery of 100 per cent. being obtained by hydrogen sulphide treatment, and acted equally well on the natural ascorbic acid of orange juice and on synthetic ascorbic acid. Dehydro-ascorbic acid was apparently not present in the intact vegetable, but was formed only when a cut or crushed vegetable containing the enzyme was exposed to air. The presence of a stabilising system for ascorbic acid, as proposed by McHenry and Graham, is not necessary, for those juices which retain their vitamin do not have any oxidase. The use of strong acids for the extraction enabled the true vitamin *C* content of the foodstuff to be obtained. If, however, the enzyme was given time to act before the acid was added, the vitamin was oxidised.

S. G. S.

Crystalline Vitamin D_4. A. Windaus and G. Trautmann. (*Hoppe-Seyler's Z. phys. Chem.*, 1937, **247**, 185–188).—Another antirachitic vitamin (D_4) has been prepared in the pure crystalline condition; the provitamin was 22-dihydroergosterol. Attempts to prepare this vitamin by hydrogenation of the compound of calciferol with maleic anhydride were unsuccessful, but irradiation of 22-dihydro-ergosterol gave a mixture from which vitamin D_4 was isolated by means of its *m*-dinitrobenzoate. The authors believe that this vitamin is related to 22-dihydroergosterol in exactly the same way as calciferol is related to ergosterol. The dinitrobenzoate melted at 135° to 136° C. (uncorr.) and had $[\alpha]_D^{18°} = +94{\cdot}5°$ in acetone. The vitamin itself had m.p. 107° to 108° C. and $[\alpha]_D^{18°} = +89{\cdot}3$ in acetone, and showed a characteristic absorption band at 265$m\mu$ with an absorption coefficient almost equal to that of calciferol. Ultimate analyses of the vitamin and its esters gave practically theoretical results. S. G. S.

Toxicological

Arsenic in a Well Water. J. Wyllie. (*Canadian Public Health J.*, 1937, 28, 128–136).—In 1922 a well was drilled to a depth of 94 feet through "red rock" (a sandy limestone stratum) to supply a farm near Madoc, Ontario, with water. As the result of drinking the water there have been several cases of chronic arsenic poisoning among the occupants of the farm. The original farmer was frequently ill and was treated for anæmia; even yet he has hyperkeratosis of the palms of his hands. In 1927 the farm was sold, and the new owner became ill, and in 1932 he was diagnosed to be suffering from nephritis, although signs of arsenic poisoning were present. He died two months later, and his brother took over the management of the farm. After two years both this brother and his sister-in-law, who had remained on the farm as housekeeper, became ill. The woman consulted a heart specialist, who diagnosed chronic arsenic poisoning, and in June 1935, the farmer underwent an operation for appendicitis. After a short period of convalescence he resumed work on the farm and very soon his former gastro-intestinal symptoms recurred. Becoming suspicious of the well water he sent samples to the Central Laboratory of the Ontario Department of Health for bacteriological and chemical analysis. The report showed that the water contained 7/10 grain of arsenic (as arsenious oxide) per gallon. An investigation of the probable source of arsenic was then made, and it was found that samples of the limestone stratum, through which the well had been drilled, contained up to 15 p.p.m. of arsenic (as As_2O_3). A thin section of the limestone, examined microscopically, showed interlocking granules of calcite with small brownish particles in the sutures between the granules, and at intervals small aggregates of similar brownish particles without definite boundaries between them and the calcite. These particles were found to consist of ferrous arsenate. Similar particles were observed in the scale from the household kettle, and a powdered sample of the scale contained 0·4 per cent. of arsenic. The clinical histories of the cases indicated that a period of approximately 2½ years was necessary before definite signs of arsenic poisoning were produced by the use of the arsenical water.

Agricultural

Boron-Content of Plants Cultivated on the Same Soil. G. Bertrand and L. Silberstein. (*Bull. Soc. Chim.*, 1937, 4, 1147–1149.)—The work here described supplements that by Bertrand and de Waal (*Bull. Soc. Chim.*, 1936, 3, 875), on the boron-content of plants grown on the same soil. The plants were grown alongside one another on a plot which had not been manured for a long time and was considered to be homogeneous in chemical composition. Ten species of agricultural plants were grown, and four weeds which occurred in the plot were also examined. All the plants were gathered just as flowering was beginning, washed, dried, and analysed as before. Some of the results were as follows:

	Ash in dry substance Per Cent.	Method	Mg. per kg. in dry substance	
			H_3BO_3	Boron
Onion ..	8·0	Colorimetric	24·4	4·3
Flax ..	7·7	Colorimetric	40·3	7·1
Celery ..	19·4	Colorimetric	67·6	11·9
			85·2	15·0
Potato ..	14·4	Colorimetric	79·0	13·9
			85·2	15·0
Bean ..	8·9	Colorimetric	87·5	15·4
			99·4	17·5
Tomato ..	20·1	Colorimetric	85·2	15·0
		Volumetric	108·0	19·0
Lucerne ..	13·0	Colorimetric	142·0	25·0
		Volumetric	164·0	28·9

Celery of the same sowing as that in the table, in its first year, contained 17·5 mg. of boron per kg. All the results now obtained fall within the previous range (2·5 to 70 mg. of boron per kg. of dry substance), and confirm the previous conclusions. Some previous results, here repeated, were:—leek (3·1), pea (21·7), purple clover (36·2), soya (37·1), lentil (41·4), scarlet runner (43) and crimson clover (70). Cereals, with the leek and onion, contain not more than 5 mg. per kg., whilst leguminous plants contain from 16·5 to 70 mg. per kg. E. B. D.

Losses of Organic Substance in the Spontaneous Heating of Alfalfa Hay. E. J. Hoffman and M. A. Bradshaw. (*J. Agric. Res.*, 1937, **54**, 159–184.)—Samples of hay were exposed in a barn in containers made from nichrome wire-cloth, a thermocouple being inserted to register the changes in temperature. One sample of cured clover or dry timothy grass (*Phleum pratense* L.) and 6 of alfalfa (*Medicago sativa* L.) containing 28 to 70 per cent. of moisture were used, and some of the baskets were placed in selected places in the mow, all of the samples being weighed and analysed before and after storage for 1 to 7·5 months under various conditions. The following analytical values are tabulated:—*Moisture.*—Comparisons of the various suggested methods of determination were made; drying to constant weight under reduced pressure at 85° to 100° C. is preferred, as no decomposition was then observed. *Ether extract.*—Ten g. of the finely-ground sample, dried as described, are extracted for 20 hours in a Soxhlet apparatus, the residue left on evaporation of the extract being dried to constant weight at 100° C. *Total sugars.*—The residue from the ether extraction is analysed by the A.O.A.C. method (*Official and Tentative Methods of Analysis*, **1930**, **1**, p. 281).

Hemicelluloses.—(*a*) The residue, after extraction of sugars, is boiled under a reflux condenser for 5 hours with 150 ml. of 2 per cent. (by weight) hydrochloric acid, capryl alcohol being added to prevent foaming. The residue is removed by filtration and washed with hot water, the combined filtrates being diluted to 250 ml. and neutralised, and aliquot portions used for the iodimetric determination of reducing sugars (*cf.* P. A. Schaffer and A. F. Hartmann, *J. Biol. Chem.*, 1920, **45**, 365). (*b*) As method (*a*) may also involve hydrolysis of the cellulose, the A.O.A.C. method (*loc. cit.*, **1**, p. 284), in which the original hay is distilled with 12 per cent. acid and the resulting furfural determined, was used, with the substitution of thiobarbituric acid for phloroglucinol to precipitate the furfural (*cf.* A. W. Dox and S. P. Plaisance, ANALYST, 1916, **41**, 384). This method is also open to the objection that uronic acids, certain aldehydes and lignin also yield furfural. A correction may be obtained, however, by applying a modification of the method of A. D. Dickson, H. Otterson and K. P. Link (*J. Amer. Chem. Soc.*, 1930, **52**, 775), in which the carbon dioxide evolved by treatment with the acid is passed through conc. sulphuric acid and then absorbed in weighed U-tubes containing ascarite; the weight of carbon dioxide, multiplied by 4, gives the weight of uronic anhydride, and, this divided by 6, gives the weight of furfural derived from uronic acids. The correction was found to be equivalent to about 25 per cent. of the total furfural. *Lignin and cellulose.*—The washed and dried residue from the previous determination (*a*) is treated by the method of Waksman and Stevens (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 167), except that the Schaffer and Hartmann method (*loc. cit.*) is used for the determination of the reducing sugars derived from the cellulose. *Nitrogen.*—The A.O.A.C. methods (*loc. cit.*, pp. 21 and 279) are preferred for the total organic, albuminoid, amino and ammoniacal nitrogen values. *Methoxyl value.*—Phillips's modification (ANALYST, 1932, **57**, 402) of the Zeisel and Fanto apparatus is recommended. *Alcohol and benzene extracts.*—The dried and weighed residue from the ether extraction is treated for 20 hours in a Soxhlet apparatus with a mixture of 32 parts of 95 per cent. alcohol and 68 parts of benzene (by vol.). The extracted material is dried for 2 days in air and then for 5 hours in the vacuum oven at 100° C., and re-weighed. *Alcohol extract.*—The dried residue from the previous extraction is re-extracted with 80 per cent. alcohol for 20 hours, and again dried and weighed. With some samples it was found preferable to use aliquot portions of the two extracts so obtained for the determination of total sugars (*cf. supra*), and portions of the alcoholic extract for the determination of lignin (*cf. supra*) and cellulose (by the method of Norman and Jenkins (*Biochem. J.*, 1933, **27**, 818). The moisture-content of the hay immediately surrounding the samples in the mows was 10 to 60 per cent., and the average moisture-content of the mows was 18 to 35 per cent. The losses in organic matter were 4 to 22 per cent. (average 13 per cent.), the highest losses being obtained when the moisture-contents of the sample and of the hay surrounding the mow were both high; variations occurred according to the position in the mow, and were probably occasioned by variations in resistance to the passage of air. When the samples had a normal moisture-content and most, or all, of the surrounding mow was relatively dry, the respective maximum losses were 8 and 8·6 per cent. (average 3·5 and 6 per cent.). The greatest losses occurred when moisture conditions favoured the production of heat, *i.e.* when the highest temperatures were recorded. The use of 1·5 per cent. of salt to inhibit spontaneous heating was without effect on the losses. When hay undergoes such losses it deteriorates considerably in quality. With two exceptions there were losses of fat (6 to 47 per cent.), which spectro-photometric tests showed to be accompanied by the complete destruction of carotene. Losses of sugars ranged from 59·1 to 93·7 per cent., and hemicelluloses, as measured by the pentosan value, decreased by 13·9 to 52·1 per cent. (by the hydrolysis method), or 4·1 to 35·7 per cent. (by the uncorrected distillation method). The greatest losses were obtained when the total loss of organic matter was greatest, and this applied particularly to the cellulose, for which losses of 6·7 to 21·1 per cent. and some gains were obtained. The lignin-contents showed very little change, whilst both gains and losses are recorded for the various nitrogen values, although the latter were only of significance where the total losses were relatively large (*cf.* Hoffman, *J. Agric. Res.*, 1935, **51**, 527). J. G.

Determination of Rotenone. W. M. Seaber. (*J. Soc. Chem. Ind.*, 1937, **56**, 168–173T.)—A series of experiments showed that rotenone was not extracted completely from derris, timbo, and "barbasco" roots by carbon tetrachloride. Extraction with cold chloroform gave higher results than with any other solvent which was tried, except ethyl acetate (*cf.* Worsley, *J. Soc. Chem. Ind.*, 1936, **55**, 349T; Abst., ANALYST, 1937, **62**, 141). A cold process is considered preferable to a hot one, as changes may occur on long heating. Beach's chloroform process (*cf. Soap*, 1936, **12**, 109), which is preferable to Rowaan's (*Chem. Weekblad.*, 1935, **32**, 291; Abst., ANALYST, 1935, **61**, 483), was carried out as follows:—Thirty g. of ground root were shaken in a flask with 300 ml. of chloroform, allowed to stand overnight, and then shaken for one hour. The liquid portion was poured off as completely as possible into a large filter-funnel (with a glass tap in the leg), which was quickly covered with a clock-glass. The liquid was filtered directly into a 200-ml. measuring flask, up to the mark. Precautions were taken to reduce evaporation to a minimum. This filtrate was transferred to a suitable flask, about 150 ml. of chloroform were distilled off, and almost all of the remainder was evaporated on a water-bath. The residue was left for a time under reduced pressure on a water-bath, and 10 ml. of filtered carbon tetrachloride were then added. The carbon tetrachloride was evaporated off first on a boiling water-bath, then at a lower temperature with a vacuum pump. After this treatment had been repeated with 5 ml. of tetrachloride, the residue was dissolved in 15 to 25 ml. of carbon tetrachloride which had been saturated with rotenone at 0° C. Rotenone was crystallised from this solution as a complex with carbon tetrachloride by Jones's method (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 23). The factor 0·72 was used to convert the weight obtained into crude rotenone. The liquid was cooled, seeded with a crystal of rotenone complex, put aside in a cool place for two days and then in ice for three hours, collected on filter-paper in a Gooch crucible, and washed with the solution of rotenone in carbon tetrachloride until the washings were pale, after which suction was continued for ten minutes. After some time the complex was stirred with a platinum rod, then left overnight supported in a rack so that there was an air space beneath. It was then stirred again, left for one hour, and re-weighed. The author does not consider any method of determination of the purity of the rotenone complex entirely satisfactory, but "pure" rotenone has been calculated approximately from the rotation of a solution of the complex in benzene, the rotation for a 5 per cent. solution of pure rotenone complex being taken as — 16·25°. When a mechanical shaker is not used for the extraction, the root may be shaken by hand with chloroform initially, then shaken occasionally throughout the next day, and on the following day before filtration. The very small error introduced into the above-described method by change of volume due to the solution of the root in the 200 ml. of chloroform tends to cancel that due to evaporation during filtration and measuring, and the resulting error is negligible. Extractions with other solvents are also described and discussed, and the results of numerous tests with various solvents are tabulated. E. B. D.

Colorimetric Evaluation of Derris Root. A. Goudswaard and J. C. Timmers. (*Pharm. Weekblad*, 1937, **74**, 630–634.)—The method of Jones and Smith (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 75) for the determination of rotenone is unsatisfactory, as the colour does not attain a constant value, and with small quantities of rotenone the results are inaccurate. The method of Danckwortt, Budde and Baumgarten (*Arch. Pharm.*, 1934, p. 561) is preferred. It is based on the observation of van Sillevoldt (*Ned. Tijdschrift Pharm., Chem. Toxicol.*, 1899, p. 246) that derris root dissolves in sulphuric acid, with the production of a blue-violet colour, and the method has been improved by Gross and Smith (ANALYST, 1934, **59**, 567) and by Goodhue (*id.*, 1936, **61**, 355). The following procedure is preferred, as it eliminates the objection noted by Danckwortt, namely, a change in the shade of the colour from yellow to brown in the first hour, and then to red-violet on standing for 24 hours. A solution of 100 mg. of the rotenone in 100 ml. of chloroform is prepared, and 0·1, 0·2, etc., to 0·5 ml. is pipetted into each of 5 similar tubes, which are then placed in the water-bath until the odour of chloroform is no longer perceptible (important). The tubes are then cooled, 10 ml. of ordinary conc. sulphuric acid (Dutch Pharmacopoeia, Ed. V) are added to each, and the colours are matched in a colorimeter. The colour ratios found for the pairs of tubes 1:5, 1:4, 1:3 and 1:2, were 8·2:40, 10:40, 14:45, and 21:45, respectively. Comparison of ordinary sulphuric acid with 0·01 per cent. solutions of a nitrate and nitrite in conc. sulphuric acid free from these impurities showed that the ordinary (Pharmacopoeia) sulphuric acid gave the best results. The others gave positive results, but the colour was not intensified by the use of larger quantities of nitrates or nitrites; additions of ammonium or iron salts were without effect. The colours obtained with extracts of derris root in chloroform also obeyed Beer's law, but the method is not considered sufficiently specific to enable the rotenone-content of derris root to be obtained (*cf.* Rowaan, *id.*, 1935, **60**, 483). The reaction may be used as a test for nitrites and nitrates if carried out with pure sulphuric acid and rotenone; it is more sensitive and more selective than the diphenylamine test. J. G.

Evaluation of the Toxicity of Derris and Mundulea. R. R. Le Geyt Worsley. (*J. Soc. Chem. Ind.*, 1937, **56**, 175–176T.)—Derris and mundulea samples can be separately evaluated from the amounts of optically active constituents in each, as determined from the optical rotation of a benzene extract of the plant under certain standard conditions (*cf.* Worsley, *J. Soc. Chem. Ind.*, 1937, **56**, 15T), by reading off from a curve for pure rotenone the percentage corresponding with the rotation. Two groups of curves are obtained by plotting these results against toxicity, the munduleas being about 2·8 times as toxic as the derrises with equal contents of optical constituents. Toxicity is determined for sprays of various concentrations; ten tests, each on ten insects, are made for each concentration. The method advocated in the previous paper (*loc. cit.*), of taking the percentage of optical constituents (there called optical dehydro-compounds) in the ether extract does not hold in general. The "toxicity ratio," or TR value, is the reciprocal of the percentage of optical constituents in the sample of root or bark. It is directly proportional to the weight of derris or mundulea to be taken to give equal toxicity. The approximate factor 2·8 can be used to compare derris and mundulea with each other. Some tentative explanations of the greater toxicity of mundulea are given, but further research on this is required. E. B. D.

Organic

Direct Determination of Oxygen in Organic Compounds. P. Goodloe and J. C. W. Frazer. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 223–225.)—A modification of the hydrogenation method of Russell and Fulton (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 384) and Russell and Marks (*id.*, 1934, **6**, 381) is proposed, in which a nickel chromite catalyst is employed in the determination of oxygen in various compounds, including nitrogen and sulphur compounds. Low results were obtained with tartaric acid and sucrose. Further work is in progress on the application of the method to compounds containing halogen. S. G. C.

Determination of Pentosans in the Analysis of Woods. I. The Gravimetric Determination of Furfuraldehyde. W. G. Campbell and L. H. Smith. (*Biochem. J.*, 1937, **31**, 535–544.)—A critical study has been made of the gravimetric determination of furfuraldehyde by means of thiobarbituric acid, and this substance is compared with phloroglucinol as a precipitant for general use in the analysis of woods. Furfurylidene-malonyl-thiocarbamide cannot be collected and washed as easily as furfuraldehyde-phloroglucide, and when certain soft woods are examined the use of thiobarbituric acid gives rise to a granular precipitate which is readily peptised during washing with cold water and cannot be collected quantitatively by the ordinary filtration procedure. In addition, the results with this reagent are uniformly high, and its use as a general precipitant for furfuraldehyde is not recommended. It is suggested, however, that diphenyl-thiobarbituric acid may prove a suitable reagent. S. G. S.

Identification of Dyes on Textile Fibres. E. Clayton. (*J. Soc. Dyers and Colourists*, 1937, **53**, 178–197.)—In view of recent advances in dyestuff technology, the work of A. G. Green and his collaborators on the analysis of dyestuffs (*The Analysis of Dyestuffs*, 1915) requires revision. The present paper is intended to supply this need, and is based on the lines of Green's original tables, 14 schemes of analysis being given. These include prints and dyeings (*a*) on cotton and other cellulosic fibres, and (*b*) on wool, silk and related fibres, each group having seven tables, *viz.* for red, orange and yellow, violet, blue, green, brown and black and grey colours. The reagents used are (1) 1 per cent. ammonia (by vol.); (2) 5 per cent. sodium hydroxide solution; (3) 5 per cent. sodium carbonate; (4) 5 per cent. ammonium chloride solution; (5) 3 per cent. hydrogen peroxide; (6) a vat-dye developer containing 8 g. of ammonium chloride and 2 g. of ammonium persulphate in 100 ml. of water; (7) a reducing agent prepared by mixing a solution of 20 g. of formosul in 75 ml. of hot water with 75 ml. of cold water and 50 g. of ethylene glycol (Formosul G); (8) commercial ethylene-diamine; (9) "developer O" (a solution of 1 g. of ammonium persulphate and 0·5 g. of ammonium dihydrogen phosphate in 100 ml. of water); (10) 1 per cent. sodium hydroxide solution. The tests are carried out in boiling-tubes on about 2 inches of the yarn or 0·5 sq. inch of cloth, and the following notes summarise the principal novel features of the tables. *Wool and Silk.*—Triarylmethane basic dyes which have been transferred from wool to cotton are readily reduced with Formosul-G (Reagent 7), and regenerated on warming with Reagent 9. Triarylmethane acid dyes, however, vary considerably in resistance to Reagent 7 and to subsequent oxidation by Reagent 9. Dyes of the Patent Blue type give most trouble in this respect, and they should be boiled for 1 minute in a 5 per cent. solution of sodium carbonate, and if the extract is deeply coloured, sodium hydroxide is added and boiling renewed until the tint is very pale; addition of glacial acetic acid then develops the original colour of the dye. Anthraquinonoid and azine acid dyes are easily reduced, the colour being restored by immersion in Reagent 5 and cold water, respectively. Most of the red and black "chrome" dyeings are distinguishable by their resistance to Reagent 7, whilst boiling 16 per cent. hydrochloric acid breaks up the lakes of azo dyes containing a co-ordinated metal, and the azo group may then be identified. Some dyes (*e.g.* Neolan Pink B) on silk require even stronger acid, and it is preferable to remove the dye from the fibre by means of warm Reagent 8, and to add sodium hydrosulphite, when permanent decolorisation takes place immediately. Almost all substantive dyes on wool or silk are detectable by boiling with Reagent 3 or 2, respectively, for 30 seconds in the presence of white cotton, which rapidly becomes stained and is then resistant to boiling Reagent 1. Exceptions to this Rule (azo dyes of the Coomassie Navy Blue and Black, or Sulphocyanine types) are identified by the dull yellow colour obtained on boiling with Reagent 10. Vat dyes change in colour in hot Reagent 7, but are regenerated by washing and aeration, or by treatment with Reagent 5. In some instances the action of Reagent 10 on a wool-dyeing forms the leuco-compound of the corresponding parent dye, which may be recognised by allowing a drop of the solution to oxidise on a filter-paper. Reagent 8 is convenient for the extraction of dyes of this type (especially indigo and its derivatives) or for the production of their leuco-compounds. The presence of azoic dyes is usually established "by difference," but unlike vat dyes, extracts of them in hot Reagent 8 are quickly and permanently decolorised by sodium hydrosulphite. *Cellulosic fibres.*—Basic dyes are best transferred to wool by boiling with 1 ml. of Reagent 2, and then adding 4 ml. of Reagent 4 and again boiling; the wool is introduced into this solution while it is cooling. Reagent 2 strips most substantive dyes which can be taken up by mercerised cotton, the new dyeing being then resistant to hot Reagent 1. Some vat dye discharges on diazotised and developed dyeings require the addition of sodium hydrosulphite to the alkali, and in others stripping is aided by Reagent 7 or 8. Sulphur dyes are identified by boiling the pattern for 30 seconds with 16 per cent. hydrochloric acid and then adding magnesium chips to the cool extract, and testing evolved gases with lead acetate paper. The usual reduction tests (*supra*) generally give positive results, but the ease with which dyes of this class are decolorised by boiling sodium hypochlorite solution (sp.gr., 1·015) is a useful distinguishing feature. Reagent 7 (hot) or 8 (cold) reduces most azoic dyes, especially if alkaline, an exception being Naphthol AS–G, which requires alkali containing a little hydrosulphite. For viscose dyeings it is preferable to use a mixture of equal volumes of 10 per cent. sodium hydroxide solution and ethylene glycol monoethyl ether (*cf.* Rowe and Levin, *J. Soc. Dyers and Colourists*, 1924, **40**, 218). They are usually distinguishable from azoic dyeings and prints by their relatively slow reactivity in the presence of cold Reagent 8. Vat dyes may be detected by heating at 60° C. with hydrosulphite in Reagent 2, and then dyeing white cotton; the original colour may be regenerated by means of a suitable vat dye developer. Since commercial samples of ethylene-diamine vary in efficiency as a reagent, it is advisable to add glucose when testing for vat dyes on cotton. Reagent 8 is a particularly effective stripping agent, and will remove even fast co-ordinated chromium lakes or substantive dyes from wool or cotton. Basic-mordant dyes (*e.g.* gallocyanine derivatives) are easily broken up by hot 5 per cent. hydrochloric acid; if the solution is made alkaline with ammonia, excess being removed by means of solid magnesium sulphate, the resulting solution will dye white wool. Chromatographic adsorption (*cf.* Cook, *Chem. and Ind.*, 1936, **55**, 721) or filter-paper tests may be used for mixture dyeings. For the former the simplest apparatus is a small vertical tube containing an adsorbing agent (*e.g.* Brockmann's activated alumina), through which is drawn by suction a solution of the dyestuff mixture. The chromatogram is "developed" by means of a suitable solvent (*e.g.* water or the usual organic solvents) which serves to break the adsorbent-adsorbate complex. The individual dyes then travel down the column at different rates and form separate zones. J. G.

Phenol Determination in Tars. E. Feil. (*Chem.-Ztg.*, 1937, **61**, 549–550.) —The following empirical method is recommended. A 4-cm. square piece of drawing paper, free from salicylic acid, is fixed to a thin wire and then dried. A tin, 90 mm. in diameter and 45 mm. high, is filled to a depth of 30 mm. with the tar-asphalt mixture under examination, and the mixture is stirred with a thermometer and heated to 100° C. The paper is quickly dipped three times into the mixture at this temperature, allowed to drip at room temperature, and hung in 200 ml. of water at 20° C. contained in a 250-ml. beaker (height 90 mm. and diameter about 60 mm.), the wire being fixed to a cork which fits the beaker tightly. The paper is removed after soaking for 24 hours. Fifty ml. of the liquid are pipetted into an elongated 100-ml. volumetric flask and the phenol is determined as follows: —Exactly 1·5 ml. of 2 *N* nitric acid and 0·2 ml. of Millon's reagent are added to the liquid, which is then warmed until it just begins to boil and is kept hot, without boiling, for 1 minute. The flask is filled almost to the mark with cold water, cooled, made up to the mark, shaken, and allowed to stand for 2½ hours. The colour developed is compared with water in a Pulfrich photometer, and the phenol-content is read from curves prepared by applying the same method of determination to a standard phenol solution containing 0·5 g. of phenol per litre. The figure obtained is multiplied by 4 to give the phenol-content of the tar-asphalt mixture. The influence, on the method, of the quantity of nitric acid, the quantity of Millon's reagent, the time of standing between making up the solution and comparing the colour, the temperature of soaking, the viscosity of the tar mixture, re-soaking of the paper in fresh water, and the exposure of the tar mixture to air has been determined. E. M. P.

Inorganic

Reduction and Electrolysis of Perrhenate. G. E. F. Lundell and H. B. Knowles. (*U.S. Bureau of Standards J. of Research*, 1937, **18**, 629–637.)—Potassium perrhenate (16·6774 g.) was dissolved in 4 litres of 2·5 per cent. sulphuric acid, and aliquot portions were passed at 5° C. through an 18-inch Jones reductor (diameter 1 inch) filled with 20-mesh granulated zinc amalgamated with 5 per cent. of mercury. The solutions were previously boiled to expel air, and the operation was carried out in an atmosphere of carbon dioxide. The reduced solutions were titrated immediately with permanganate, or they were caught in excess of ferric sulphate or permanganate and then titrated. All the results indicate that the perrhenate is reduced to hydrorhenic acid: $HReO_4 + 8H = HRe + 4H_2O$. If the reduced solution, protected from oxygen, is warmed moderately and left to itself for 30 to 60 minutes, the reaction $HRe + H_2SO_4 = HReO + H_2O + SO_2$ appears to take place, with formation of hyporhenous acid.

Rhenium was deposited as such when a perrhenate solution containing 5 per cent. of sulphuric acid was electrolysed overnight between a sand-blasted platinum gauze cathode and spiral anode at 0·25 amp. per sq. dm. and 2·34 volts. The deposits were washed with water, alcohol and ether, and dried for 10 seconds at 105° C. Direct weighing of the deposit gave a positive error due to oxidation. The deposited metal does not oxidise appreciably in perfectly dry air, but it oxidises very rapidly in moist air, being quantitatively converted into perrhenic acid within 24 hours. The element can be determined by electro-deposition, conversion into perrhenic acid by exposure to moist oxygen, and alkalimetric titration of the perrhenic acid (phenolphthalein indicator). The small amount of rhenium that may escape deposition may be determined colorimetrically by Hurd and Babler's method (ANALYST, 1936, **61**, 500). W. R. S.

Electro-deposition of Zinc from Citrate Solution. R. Winchester and L. F. Yntema. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 254–256.)—The zinc should be present in sulphate solution free from heavy metals, but aluminium, chromium and magnesium may be present. The solution, to which 1·5 g. of citric acid is added, is rendered neutral to methyl red—methylene blue indicator with sodium hydroxide. It is diluted to 200 ml. and electrolysed with a copper or copper-plated gauze cathode and a rotating platinum anode, the cathode current density being about 1 amp. per sq. dm. After 1½ to 2 hours, a 1-ml. sample of the electrolyte is tested by the addition of 0·5 ml. of saturated hydrogen sulphide water. The electrolysis should be continued if more than a faint opalescence is produced. Finally the cathode is withdrawn and washed without switching off the current, dried and weighed. Practically quantitative results were obtained with 0·2 g. of zinc taken. Nitrate ions, dimethylglyoxime and urea interfere, also the following metals:—antimony, arsenic, bismuth, cadmium, copper, iron, lead, manganese, mercury, nickel and silver. S. G. C.

Separation of Zinc from Cobalt by means of Hydrogen Sulphide. E. A. Ostroumow. (*Ann. Chim. anal.*, 1937, **19**, 145–152.)—Zinc sulphide precipitated by hydrogen sulphide from buffered acid solution tends to be much contaminated with cobalt if that element is present. Under similar conditions the entrainment of iron, manganese and nickel was much less marked. The particular behaviour with cobalt is attributed to post-precipitation. The effect can be reduced by the presence of acrolein in the liquid, which is considered to become adsorbed on the zinc sulphide particles and to take the place, to some extent, of the active layer of adsorbed hydrogen sulphide which is held to be responsible for post-precipitation phenomena. It was further found that a slow current of hydrogen sulphide was desirable for minimising post-precipitation, the passage of the gas being continued only long enough to secure coagulation of the precipitate. A method suitable for a solution containing moderate amounts of zinc and cobalt (0·05 to 0·1 g.) is as follows:—The solution is neutralised approximately with dilute sodium hydroxide solution, and 10 ml. of chloroacetic acid (190 g. per litre) are added. To the clear liquid 10 ml. of sodium acetate solution (136 g. per litre) are added, and the solution is diluted to 150 ml. and heated (temperature not stated). Five ml. of acrolein solution (4 per cent.) are added, and a slow current of hydrogen sulphide (about 60 to 80 bubbles per minute) is passed into the solution until the zinc sulphide coagulates (about 25 to 30 minutes are usually sufficient). The zinc sulphide is filtered off, washed with dilute acetic acid (4 per cent.) saturated with hydrogen sulphide, and burnt off. The residue is converted into zinc sulphate in the usual way and weighed. Practically the theoretical recovery of zinc was obtained in test experiments, and the amount of cobalt in the zinc sulphate was found by colorimetric tests to be less than 1 mg. With small amounts of zinc in presence of moderate amounts of cobalt, difficulties were experienced, because the precipitate did not coagulate well and was difficult to filter off. The addition of paper-pulp suspended in water was satisfactory for collecting the precipitate, but was found to lead to serious contamination of the precipitate with cobalt. It was concluded that this partial precipitation of cobalt was due to a kind of post-precipitation on the paper fibres promoted by the fact that the water absorbed in the added paper gave locally too low an acid concentration. This drawback could be avoided by using pulp saturated with a buffered acid solution as follows:—Paper pulp prepared in the ordinary way is filtered off on a Buchner funnel, and then shaken up with 150 ml. of water containing 10 ml. of chloroacetic acid solution (190 g./litre), 10 ml. of sodium acetate solution (136 g./litre) and 5 ml. of acrolein solution (4 per cent.); quantities of this suspension are filtered off, as required, and the impregnated paper is added for the purpose of collecting the zinc sulphide. With amounts of zinc of the order of 0·5 to 5 mg. in the presence of 0·1 g., of cobalt, it is desirable to pass hydrogen sulphide for about 15 minutes after the first signs of precipitation are seen; the impregnated paper pulp is added, and the passage of the gas is continued for a further 40 minutes, the determination being finished off as before. Quantitative results were obtained with zinc in amounts down to 0·5 mg. S. G. C.

Separation of Beryllium in the Presence of Complex Tartrates. H. S. Miller. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 221.)—Beryllium may be precipitated from complex tartrate solution by the addition of a regulated quantity of ammonia. In this way it was possible to separate beryllium fairly quantitatively from elements, such as aluminium, iron, copper and chromium, that form complex tartrates from which the hydroxide is not precipitable by ammonia. No general directions for carrying out the method are given. The precipitate of beryllium hydroxide obtained is gelatinous and is stated to suffer from the disadvantage of readily adsorbing other substance from the solution, making repeated re-precipitation necessary. S. G. C.

Phosphotungstate Colorimetric Method for the Determination of Vanadium. E. R. Wright and M. G. Mellon. (*Ind. Eng. Chem. Anal. Ed.*, 1937, 9, 251–254.)—The reaction on which the method is based involves the addition of sodium tungstate and phosphoric acid to an acid solution containing quinquevalent vanadium, whereupon a yellow or brownish colour is produced varying in hue and intensity with the vanadium concentration (*cf.* Willard and Young, *Ind. Eng. Chem.*, 1928, **20**, 764; Abst., ANALYST, 1928, **53**, 674). The preferred concentrations of reagents in the colorimetric solution are 0·025 *M* sodium tungstate, 0·5 *M* phosphoric acid and 0·6 *N* nitric, sulphuric, hydrochloric or perchloric acid; the concentrations are not critical; the amount of vanadium present in 100 ml. should be between 0·02 and 10 mg. Heating the solution to boiling is necessary for the full development of colour if more than 1 mg. of vanadium is present per 100 ml. The following substances were found to have no effect on the colour (in 100 ml. volume): sodium chloride (3 g.); sodium nitrate (5 g.); magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminium, lead, arsenic, bromine, and acetate ion (0·5 g.); beryllium (0·025 g.); silver, lithium, chlorate ion, oxalate ion, citrate ion, tartrate ion (0·1 g.); silicate ion (0·05 g.); cyanide ion (0·02 g.). Ammonium and potassium give precipitates with the phosphotungstic acid and must not be present in more than traces. The following interfere by producing a precipitate: antimony, tin, titanium and zirconium, only small amounts of these being tolerable. Molybdenum tends to interfere, when present in fairly large amount, by forming a coloured compound. Ferric iron in the form of chloride gives a brown colour.

The following method is proposed for steel:—(*a*) *Chromium-Tungsten Steels containing* 0·7 *to* 2·0 *per cent. of Vanadium.*—A 150-mg. sample is dissolved, as far as possible, in 10 ml. of hydrochloric acid (1:1), by heating. Nitric acid is added, drop by drop, in amount sufficient to oxidise iron and tungsten. Perchloric acid (7 ml. of 60 per cent. acid) is added, and the liquid is evaporated until fumes of perchloric acid are evolved, and kept boiling for 2 to 3 minutes after the orange-red colour, due to chromic acid, has appeared. After cooling, 40 ml. of water are added, the liquid is boiled, and 5 ml. of 0·5 *M* lead perchlorate solution are added. The precipitate of lead chromate and tungstic acid is filtered off from the cold solution, washed with a little cold water, and rejected (the small amount of vanadium occluded in the tungstic acid is ignored in this method). To the filtrate are added 10 ml. of nitric acid (1:1), 3 ml. of phosphoric acid (90 per cent.) and 5 ml. of 0·5 *M* sodium tungstate solution, the solution is heated to boiling, cooled, and diluted to 100 ml. The colour is compared colorimetrically with that of a solution containing 1·5 mg. of vanadium (as sodium vanadate), the same amount of reagents and about 60 ml. of water, which has been heated to boiling, cooled and diluted to 100 ml. (*b*) *Chromium-Tungsten Steels containing* 0·1 *to* 0·7 *per cent. of Vanadium.*—A 0·5-g. sample is dissolved, as far as possible, in 20 ml. of hydrochloric acid (1:1) by heating, 0·5 ml. of nitric acid is added, the liquid is evaporated to 10 ml., 5 ml. of hydrochloric acid are added, and the liquid is transferred to a separating funnel with not more than 5 ml. of water. The bulk of the ferric chloride is extracted by means of 30 ml. of ether. The aqueous layer is heated to remove dissolved ether and evaporated to fuming with 7 ml. of 60 per cent. perchloric acid, and the method continued as in method (*a*). S. G. C.

Determination of Potassium in Soils and Silicates. J. E. Gieseking and H. J. Snider. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 232–233.)—A new flux is proposed for effecting the decomposition of soils, clays and similar materials when potassium is to be determined. It consists of a mixture of two parts of sodium carbonate with one part of lithium carbonate, and melts between 470° C. and 480° C. Potassium is finally determined by the cobaltinitrite method. A 1-g. sample of the 100-mesh material is first heated in a platinum capsule with perchloric acid in order to destroy organic matter. After removal of the perchloric acid by heating, the residue is mixed with 8 parts of the flux and covered with a layer of it. The mixture is fused at 500° to 600° C., with the capsule covered, until bubbling has ceased. The cooled melt is dissolved, as far as possible, in 75 ml. of 4 *N* hydrochloric acid; the liquid is evaporated to dryness, 10 ml. of conc. perchloric acid are added and evaporated to dryness. The perchloric acid treatment is repeated with the addition of 1 ml. of conc. hydrochloric acid, and 0·5 ml. of nitric acid to assist in dehydrating the silica and to decompose any traces of ammonium salts present. The residue is digested for a few minutes with 50 ml. of 5 per cent. hydrochloric acid, and the silica is filtered off, washed with 2 *N* hydrochloric acid, and ignited in the original crucible; the silica is volatilised with hydrofluoric acid and a little perchloric acid, and any residue is dissolved in a little dilute hydrochloric acid and added to the main solution, in which the potassium is now determined by the cobaltinitrite method, that described by Volk and Truog (*J. Amer. Soc. Agron.*, 1934, 26, 537) being suitable. S. G. C.

Determination of Rare Alkalis. J. C. Hillyer. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 236.)—The author discusses the applicability of Wells and Stevens' method (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 439) to the analysis of the mineral pollucite, which contains over 30 per cent. of caesium oxide. A modified solvent-mixture is proposed for separating the alkali chlorides. It consists of 0·4 ml. of water and 10 ml. of alcohol, both saturated with hydrogen chloride, and will dissolve the following amounts of alkali chlorides at 25° C.:—potassium chloride, 0·0006 g.; rubidium chloride, 0·0027 g.; caesium chloride, 0·024 g. S. G. C.

Analysis of Pollucite. R. C. Wells and R. E. Stevens. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 236–237.)—The authors concur in the necessity for modifying their original method in dealing with samples containing a high proportion of caesium and indicate a further procedure applicable to pollucite (*cf.* preceding Abst.). This mineral, which occurs at Tin Mountain, S. Dakota, is unique, as it is the only mineral compound of caesium found in nature. Caesium may replace potassium in minerals, but its amount seldom exceeds a few units per cent. and usually it is absent. S. G. C.

Determination of Silicon in Aluminium and Aluminium Alloys. H. V. Churchill, R. W. Bridges and M. F. Lee. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 201–202.)—In order to examine the question whether silicon is lost as hydride when aluminium alloys are dissolved in acids, a number of representative aluminium alloys in different conditions of heat-treatment were submitted to three methods for the determination of silicon, involving attack with (*a*) sulphuric-nitric-hydrochloric acid mixture, (*b*) perchloric acid, and (*c*) sodium hydroxide. The results obtained by the tri-acid and sodium hydroxide methods showed satisfactory agreement for the silicon-contents of commercial aluminium, aluminium-manganese alloy (Mn, 1·25 per cent.), straight aluminium-silicon alloy (Si, 5 per cent.) and duralumin (Mn, 0·5; Cu, 4·0; Mg, 0·5 per cent.), irrespective of heat-treatment. Except with the material in the fully annealed condition, marked differences were found between the results of these two methods with aluminium alloys containing magnesium-silicide hardener* (*e.g.*, Mg, 0·6; Si, 1·0 per cent.). Examples of the results obtained with such an alloy are as follow:

	Silicon, per cent.		
Heat treatment	Tri-acid method	Perchloric acid method	Sodium hydroxide method
Fully annealed	0·93	0·92	0·94
"Solution heat-treatment"	0·85	0·75	0·94
"Solution heat-treated and aged at room temperature"	0·89	0·84	0·94

There was a general trend towards low results with perchloric acid attack with all the materials tested. It was concluded that, whilst the tri-acid method is usually satisfactory, the sodium hydroxide method should be used when aluminium-magnesium silicide alloys are analysed for silicon. The following methods were found satisfactory at the American Aluminium Research Laboratories:

Tri-acid method.—A 1-g. sample, contained in a 250-ml. beaker, is attacked with 35 ml. of acid mixture (485 ml. of water, 115 ml. of sulphuric acid, 200 ml. of hydrochloric acid and 200 ml. of nitric acid). When no further action is evident, the liquid is evaporated until heavy fumes of sulphuric acid are evolved, the heating then being continued for 15 minutes. After cooling, 10 ml. of 1 : 3 sulphuric acid and 100 ml. of hot water are added, and the mixture is heated until the metallic salts are dissolved. Some paper-pulp is added and the residue is filtered off and washed with hot water. The filtrate is evaporated again as described above, in order to recover traces of silica, which are ultimately added to the first precipitate, the combined filters being ashed in a platinum capsule and the residue ignited. The residue is fused with 1 to 8 g. of sodium carbonate, and the cooled melt is dissolved in 50 ml. of 1 : 3 sulphuric acid. The solution is evaporated, and the residue is heated for 15 minutes while dense white fumes are evolved. The cooled residue is dissolved, as far as possible, in 100 ml. of hot water, prolonged digestion being avoided to minimise re-solution of silica. After the addition of paper-pulp, the silica is filtered off, and the filtrate is evaporated as before to recover traces of silica, which are then combined with the main portion. The filters are ashed in a platinum capsule, and the residue is ignited at 1000° C., cooled and weighed. It is moistened with a few drops of dilute sulphuric acid, hydrofluoric acid is added, the liquid is evaporated to dryness, and the residue is ignited and weighed. The difference between the two weights represents silica. A blank determination on the reagents is advised.

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* *Abstractor's Note.*—The alloy silmalec is a representative of this class of alloy in this country.

Sodium hydroxide method.—A 0·5 to 1·0 g. sample is dissolved, in a covered Monel-metal beaker, in 15 ml. of 30 per cent. sodium hydroxide solution. The liquid is then evaporated to 5 ml. If the solution is dark in colour, 2 to 3 ml. of 3 per cent. hydrogen peroxide are added, the liquid being then re-evaporated to 5 ml. The solution and any insoluble matter are transferred to a Pyrex beaker containing 65 ml. of 1 : 1 sulphuric acid and 20 ml. of 60 per cent. perchloric acid. The silica is recovered and determined in the usual way, with re-evaporation of the filtrate and use of the hydrofluoric acid volatilisation process. An alternative process is described involving acidification of the sodium hydroxide solution with hydrochloric acid, and evaporation with perchloric acid, as published by the Aluminium Research Institute (Standard Methods for Sampling and Analysing Aluminium and certain Aluminium Alloys, 1932). (*Cf.* Callender, ANALYST, 1933, **58**, 81.)

S. G. C.

Colorimetric Determination of Silicic Acid in the presence of Iron, Phosphorus and Fluorine. I. P. Alimarin and V. S. Sverev. (*Mikrochem.*, 1937, **22**, 89–101.)—The Diénert and Wandenbulcke method (*Compt. rend.*, 1923, **176**, 1478; Abst., ANALYST, 1923, **48**, 398) which consists in comparing the yellow colour formed from silicic acid and ammonium molybdate with a standard solution has been tested under various conditions. For visual comparison the lowest concentration for accurate matching is about 1 mg. per litre, and the highest 50 mg. per litre. For the comparison, varying amounts of standard sodium silicate are treated with 2 ml. of a freshly prepared 10 per cent. solution of ammonium molybdate for every 5 mg. of silica present, and 4 drops of 50 per cent. (by vol.) sulphuric acid, to bring the *p*H to about 1·2–2·0. The solution is then diluted to 100 ml. The colour reaches the maximum in 10 minutes at room temperature. A more intense and constant colour is produced if the solution is heated on the water-bath for 5 minutes. The intensity obtained at 50° to 66° C. remains constant for 24 hours. The acidity of the solution is important and should be maintained within the stated limits of *p*H 1·2 to 2. Excess of mineral acid may be eliminated by buffering with sodium acetate and acetic acid. Ammonium molybdate should be added before the acid; this is especially important in dilute solutions of silica. Iron, if not present in excess of 20 mg. per litre, does not interfere. To remove excess of iron the best results are attained by fusing the substance with sodium carbonate and leaching the melt with a sodium carbonate solution, all the iron remaining in the residue and all the silicic acid passing into solution. The yellow colour given by phosphates reaches its maximum at 60 mg. of P_2O_5 per litre, and disappears if the P_2O_5 content is increased beyond 100 mg. per litre. If oxalic, citric or tartaric acid is added after the colour formation the yellow colour due to phosphate is destroyed, whilst that from silicic acid persists for several hours. In the presence of phosphorus and iron it is proposed to add to the coloured solution an excess of phosphoric acid, which destroys the colour of phosphomolybdate without affecting that of silicomolybdate, and which also combines with the iron present to form a colourless undissociated phosphate. The procedure is as follows:—Sodium acetate is added to neutralise any mineral acid present, then 2 ml. of 98 per cent. acetic acid, and for every 5 mg. of silica, 10 ml. of 10 per cent. ammonium molybdate are added. The solution is heated to 50° to 60° C. for 5 minutes, and after cooling and dilution 1 ml. of phosphoric acid (sp.gr. 1·7) is added. The coloured solution is diluted to 100 ml. and compared with a standard solution of sodium silicate treated by the same method. The colour persists for 30 minutes. The influence of the fluoride ion is eliminated by introducing aluminium chloride into the solution. If the fluoride tested is insoluble in water it may be dissolved in 10 ml. of 10 per cent. aluminium chloride solution, after which the other reagents are successively added. J. W. M.

Studies in Fluorine Distillation. D. Dahle and H. J. Wichmann. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 297–303.)—The authors' previous work on the influence of certain factors on the recovery of fluorine by distillation with sulphuric acid (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 313) is extended to include distillations with perchloric and phosphoric acids. The effect of the presence of the salts of non-volatile acids is also studied. To determine the effect of "input volume" (*i.e.* the volume of liquid present in the distillation flask when the temperature at which the distillation is to be made is reached), mixtures of perchloric acid with water giving different input volumes but containing the same amount of sodium fluoride were distilled at constant temperatures, *viz.* 125° C. and 135° C. to a constant output volume of 25 ml. The input volume was varied in two ways, *viz.* by increasing the amount of acid and by adding salts of non-volatile acids (sodium perchlorate and calcium monophosphate). The amount of fluorine present in each experiment was 0·5 mg. The effects of the two methods of changing input volume are compared, and a similar comparison is made for sulphuric acid with sodium sulphate and ammonium persulphate. From the data obtained the following conclusions are drawn. The fluorine recovery decreases with increasing input volume; the change in recovery decreases with increasing input volume; the presence of soluble salts of non-volatile acids causes a decrease in the fluorine recovery by a greater amount than is indicated by the corresponding increase in input volume. This retarding effect of soluble salts becomes important when material low in fluorine-content is to be analysed and relatively large quantities of sample must be used. The effect of input volume is almost twice as great when perchloric or phosphoric acid is used as when sulphuric acid is used. This is of practical interest when complete recovery in the smallest possible amount of distillate is required. Perchloric and sulphuric acids cause a more rapid rate of volatilisation of fluorine than does phosphoric acid. Comparisons made at constant input volumes show that both sulphuric acid and perchloric acid are more efficient at 125° C. than phosphoric acid at 135° C. This is of practical interest in the problem of the removal of fluorine from commercial phosphoric acid, as well as in the substitution of this acid for the other acids in distillation. The effect of varying temperature is the sum of two effects working in the same direction, *viz.*, the decrease in input volume and the rise in temperature. By deducting the first-named effect, which can be estimated at least approximately, the second effect is found. Apparently the recovery is greater if the distillation is carried out at higher temperatures. The temperature effect per degree is greater when large volumes are present during distillation than with small volumes. The temperature effect at similar input volumes is about twice as great for perchloric acid as for sulphuric acid, whilst phosphoric acid occupies an intermediate position. As with fluorine distillations with sulphuric acid, the quantitative recovery varies with the amount of distillate collected in accordance with the following equation—

$$K = \frac{1}{t} \log \frac{c}{c - x}$$

where K is a constant, t is the number of ml. of distillate collected, c is the original concentration of fluorine, and $(c - x)$ is the concentration in the residue remaining in the flask after t ml. has been distilled. If c is taken as 100, x becomes the percentage recovery in t ml. of distillate. A. O. J.

Hydrolysis of Rock-forming Minerals. A. Bramall and J. G. C. Leetch. (*Bull. Inst. Min. and Met., No.* 391, April, 1937.)—Finely-divided powdered minerals are found to be very hygroscopic, and in the hydrolysed form many minerals are partly soluble in water; often alkali is leached out, and a mineral differing in structure from the original mineral may be obtained. A simple method of testing the solubility of a mineral to water is to grind it up very finely and test the reaction of the powder in water. Most of the common rock-forming minerals are reactive, *e.g.* various basic micas, hornblendes and other amphiboles (including asbestos); wollastonite, diopside, hypersthene, augite, aegirite, and other pyroxenes; olivine, apatite, sphene and some varieties of tourmaline; grossularite, melanite and some varieties of almandite; members of the chlorite and epidote groups; calcite, aragonite, magnesite, dolomite; brucite and chondrolite. Sericite, hydromuscovite and true muscovite are among the less reactive species. The reactivity and hygroscopic properties of the finely-divided dust may be explained from a knowledge of the crystal structure, and throw light on the problems of solubility of fine dust (*cf.* p. 645). J. W. M.

Physical Methods, Apparatus, etc.

Photographic Method for the Detection of Thorium Oxide in Lamp Filaments. J. A. M. Van Liempt and J. H. M. Van Uden. (*Rec. Trav. Chim. Pays Bas*, 1937, **56**, 607–612.)—The method depends on the blackening of a photographic plate by radioactive thorium compounds in tungsten or molybdenum filaments (*cf.* Behrens-Kley, *Mikrochemische Analyse*, 1915, Pt. 1, p. 115). After removal of grease by treatment with hot sodium hydroxide solution the filament is wrapped once round a glass plate (9 × 12 cm.), and then secured on one surface so that the other glass surface is in contact with it. A photographic plate is placed on this surface in such a way as to make close contact with the wire, pressure being avoided in order to prevent damage to the plate. Hilger–Schumann plates gave the best results; after one day filaments containing 1 per cent. of thorium oxide produced no visible stain, whilst those with 2 per cent. produced a slight stain; in 5 days filaments containing 1 and 3 per cent. of the oxide produced a moderately dark stain and an intense stain, respectively. The next best results were obtained with ordinary sensitised plates (H and D, 4400), a slight darkening being obtained from 3 per cent. of oxide after 3 days. A metol-hydroquinone developer, or the developer recommended for the plates concerned, was used. Drawn filaments gave a greater degree of blackening than filaments which had been recrystallised by heating at 2200° C. for 1 hour, or than single-crystal filaments. This supports the authors' earlier conclusions (*Z. anorg. Chem.*, 1927, **168**, 107; 1930, **193**, 144) that the thorium in drawn filaments is held between the fibres, and also that a crystalline structure tends to enclose it. Recrystallisation by heating at 2900° C. for 8 hours produced no change in the degree of blackening, although an examination of the residue remaining after solution of the filament in a mixture of nitric and hydrofluoric acids showed that reduction to the metal had taken place. The phenomenon is therefore atomic in character. Moreover, filaments from pure thorium produced an intense darkening after 1 day, even when the ordinary sensitised plate was used and the diameter was only 150μ. The sensitiveness is increased if the surrounding atmosphere is moist and if the diameter of the filament is relatively large; thus, a 300-μ filament containing 1 per cent. of oxide required 2 days to produce slight blackening, whilst filaments having diameters of less than 50μ required 18 days or longer in which to produce similar effects. The effects of low pressures (down to 0·1 mm.) are negligible.

J. G.

Photometric Determination of the Colour of Cooked Potatoes. P. Bilham, A. E. Maunsell and L. H. Lampitt. (*J. Soc. Chem. Ind.*, 1937, **56**, 165–168T.)—The colour of cooked potatoes depends on two factors. One is the normal potato colour, from white to yellow; the other is a grey tinge which may be normal or may develop, through some abnormality, on cooking. To obtain a grading system for potatoes which tend to blacken on cooking, a photometric method of determination of greyness is preferable to one with the unaided eye, as the yellow colour of some potatoes tends to mask the effect of blackening. The colour of the potato is matched against one of a series of standard yellow cards, and greyness is measured by the diminution in the amount of reflected light from the card which is required in order to match that from the sample in intensity. Six cards, numbered from 1 to 6, cover the range from creamy white to deep yellow in approximately equal steps. Grading for greyness is as follows:

Diminution in reflection, per cent.	0	1–4	5–9	..	55–59
Grade No.	0	½	1	..	6

The Zeiss–Pulfrich instrument was used for this work. Two beams of light, obtained from the same lamp by means of mirrors, were focussed by means of lenses and directed at an angle of 45° on to the horizontal surfaces of the sample and card. Representative potato samples were prepared by hand and boiled in batches of six, one sample from each batch being included in the next batch in order to detect any abnormality in conditions of cooking. When the centres were soft, but before the outside began to break up, the potatoes were removed and mashed by forcing them through a grid with holes 2 mm. in diameter. After thorough mixing, a representative sample was packed in a Petri dish (95 mm. in diameter, 14 mm. in depth), the surface was smoothed with a knife, and the yellow colour was matched with a colour-card. The intensity of light from the card was then regulated by the drum of the photometer, and the grade number for greyness obtained. Four different parts of the surface of the sample were examined and the mean was taken. If the tint was between that of two yellow cards, four observations were made with each, the intensity was taken as the average of the eight, and the yellow grade number as half-way between the two card-numbers. Reproducibility of results was tested with mixtures of any two samples of white, white-grey, yellow, and yellow-grey potatoes in various known proportions by weight. Results of grading directly and by calculation are compared, and graphs for percentage composition against (*a*) percentage reflection and (*b*) yellow and grey grade numbers are given and discussed. These show that no mixture examined was placed in a grade that would theoretically be wrong by more than half a unit. E. B. D.

Sampling of Industrial Dusts by means of the "Labyrinth". H. V. A. Briscoe, J. W. Matthews, P. F. Holt and P. M. Sanderson. (*Bull, Inst. Min. and Met.*, No. 393, June, 1937.)—The "labyrinth" is an apparatus designed for the collection of comparatively large samples (of the order of 10 to 300 g.) of dust from the air of mines and factories. The apparatus consists of a long cylindrical or rectangular box containing baffles consisting of a series of polished copper plates, spaced and located by lengths of copper tube and held together in a single assembly by long brass bolts and wing nuts. In the rectangular shape the box is 36 in. × 6 in. × 4 in., and the baffles, which are spaced 1 in. apart, have an area 6 in. × 3¼ in., leaving a space 6 in. × ¾ in. above or below each baffle. The box can easily be taken apart, leaving the dust undisturbed. If required, dust from each section may be collected separately. The cylindrical model is stronger, the cylinder being a 14 s.w.g. copper tube, 36 in. long × 3 in. internal diameter. To permit of the easy removal of the collected sample, the baffle assembly is wrapped with an overlapping sheet of celluloid, held in place by woollen yarn. Connections are made by short lengths of inner tube. In a test experiment, a labyrinth was connected with a 3-in. opening in the suction duct close to a high-pressure fan, ventilating a flint-grinding plant. To avoid the collection of many large particles, the entering air was drawn through an improvised elutriator made from an iron drum. After being left for 25 days (500 working hours), when the flow was of the order of 1000 m^3 per hour, a sample of about 100 g. of dust was collected. No attention was required except for setting up and dismantling. Several trials showed that over 50 per cent. of the dust was normally collected in the first sections, the last sections collecting less than 1 per cent. of the total weight. Samples of graded particle size are collected, the last sections consisting entirely of particles of 5μ and less. The efficiency of collection depends on the rate of flow, the faster rate being more efficient up to about 95 per cent. The advantages of the labyrinth, which is being used in an investigation of dangerous dusts, are that the dust is collected in an unchanged form without being heated or wetted. Sixteen photomicrographs are given showing the variation in particle size of various dusts collected in the different sections. J. W. M.

New Properties of Certain Dusts. H. V. A. Briscoe, J. W. Matthews, P. F. Holt and P. M. Sanderson. (*Bull. Inst. Min. and Met.*, No. 393, June, 1937.)—Samples of certain industrial dusts collected in the labyrinth (see preceding abstract) were examined for solubility in water under controlled conditions. The dusts were calcined flint, asbestos, cement and sillimanite; of these, the first two are extremely dangerous, the latter two, so far as is known, are innocuous to man and do not cause silicosis. The soluble silica, extracted by treating 1 g. of dust with 100 ml. of water at 100° C. for 5 hours, was as high as 12 mg. per 100 ml. for the flint dust of smallest particle size, 30 mg. per 100 ml. for the most soluble asbestos dust, and only 1 mg. per 100 ml. for cement and sillimanite. Experiments on pure graded quartz showed that the "solubility" increased with decreased particle size, increased with rise of temperature and time of extraction, and varied with variation in weight ratio of solid to solvent, so that no absolute solubility figure is obtainable, and to obtain comparative results the conditions must be strictly controlled. The effect of addition of various other substances on the solubility of silica is being investigated. The addition of lime or cement in equal weight to asbestos, quartz or flint dust decreased the solubility of the silica to a value equal to that given by cement alone (1 mg. per 100 ml.) or less. Of other calcium compounds tested, only calcium borate was at all efficacious, the soluble silica in asbestos being reduced from 42 mg. per 200 ml. to 8 mg. per 200. Magnesia behaves similarly to lime. Cryolite (Na_3AlF_6) diminishes the yield of soluble silica from flint and asbestos, but increases the yield from kaolin, felspar, cement and quartz. Sugar charcoal markedly depresses the yield of soluble silica from quartz, but has no effect on asbestos, flint, orthoclase and kaolin. Comparative solubilities of asbestos, flint (pure), quartz, felspar, sericite and kaolin showed that the largest amount of dissolved silica is yielded by asbestos and flint.

J. W. M.

Reviews

The Scientist in Action: A Scientific Study of his Methods. By William H. George, M.Sc., Ph.D., F.Inst.P., Royal Society Sorby Research Fellow, and Honorary Lecturer in Physics, University of Sheffield. Pp. 355. London: Williams & Norgate, Ltd. 1936. Price 10s. 6d. net.

The author defines scientific research as a form of human action which gives two typical products—facts, and the arrangement of facts.

Facts are observations regarding which general agreement can be attained—that is to say, that any person repeating the observation in the exact circumstances in which it was made will obtain the same result. The only class of observations which fulfil this requirement are coincidence observations—the coincidence of the end of the mercury column with a mark on the thermometer, of the liquid in a burette with a mark on the scale, of the colours of two coloured liquids, and so on.

Scientific classifications, laws or theories, are arrangements or "patterns" into which a number of facts will fit. Such "patterns" are said to "explain" the facts; but they are to be regarded as tentative, not necessary, for it is always possible that some other "pattern" may equally fit the known facts. Other facts may be discovered which will not fit into the pattern, and a new pattern may be devised into which all the facts may be fitted. To this process there can be no finality.

All research work must have the quality of "newness." The new theory or pattern must not be merely an extension of the old, but a new way of regarding the facts—the idea, for example, of looking at disease as due to the absence of some essential factor from food, instead of the presence of some disease-causing factor.

The scientific investigator must banish from his mind the idea of "absolute truth " as an end to be attained by research; he must make no statements about how things "should" or "ought to" behave, to which we are so prone in discussing the ordinary occurrences of daily life; nor must he give way to the habit of "assessing values " and assert that one "pattern" is "better" than another, or "the best."

Throughout, the observer is as much a part of the phenomenon as the observed; science has no concern with the question whether the things observed would or would not still remain were there no human race; and as all our observations depend upon our sensuous impressions, we must be alive to the imperfections of our senses.

These things are discussed in a series of chapters:—The eye-witness's observation; Scientific observation; Pattern; Are facts first seen in isolation?; Selection and abstraction; Order, laws, and classification; Pattern in action; The scientific theory; Some problems of theorising; Some factors in experimental technique; The future of experimental research. The book ends with a statement of the author's personal attitude, a summary of the contents, and a bibliography.

No adequate account of the book can be given in any short review; it must be read to acquire a knowledge of its contents. The present reviewer has found it a difficult book to read—a little prolix and repetitory—and feels that the presentation might have gained in clearness if made in considerably fewer words; but perhaps this is a personal idiosyncracy, and others may find the wealth of illustrative exposition a help to the understanding of the argument. It is a book that has obviously been written because the author felt that he must write what he had thought, not think what he must write; and like all such books, it will excite thought in the reader. J. T. DUNN

ENZYME CHEMISTRY. By HENRY TAUBER, Ph.D. Pp. 243. New York: John Wiley & Son, Inc.; London: Chapman & Hall, Ltd. 1937. Price 15s. net.

The enzymes—the agents by which the living cell is able selectively to accelerate certain chemical reactions, hydrolytic, synthetic or oxidative-reductive, which are essential to the functional activity or well-being of the tissues—have a strong appeal to the imagination of chemists in virtue of their astonishing activity, and their study is obviously of fundamental importance if effective knowledge is to be obtained of both physiological processes and pathological changes occurring in living matter.

This joint appeal has led, during the past thirty years, to an ever-increasing amount of experimental activity in this field, and it is doubtful whether we have even yet reached the second inflexion of the curve. Whereas in 1907 the whole field of existing information regarding the enzymes could have comfortably been dealt with in a relatively few pages, in 1937 five thousand pages of "Oppenheimer" are needed to summarise our knowledge, and an annual volume of about 350 pages, "Ergebnisse der Enzymforschung," struggles manfully to keep biochemists and others abreast of the main lines only of advance.

To compress more than a small part of even the very recent developments in enzyme chemistry into some 240 pages, as has been attempted by Tauber, is a task which could only succeed by using what might well be called "review of reviews" methods, supplemented by copious references to original papers and to more specialised reviews, by rigid elimination of reference to most of the earlier work (with the tacit assumption that this work is probably known to the reader), and by abstaining from critical appraisal. The author indeed makes no claim to completeness, and has deliberately reduced theoretical considerations—such as those dealt with fairly recently in Haldane's monograph—to a minimum.

He has nevertheless succeeded in this volume in bringing together valuable, and in places even detailed, accounts of many of the recent significant researches in this field, and that in such a way as to provide a well-documented and very readable summary. The chemist with no specialised knowledge of enzyme work will be able to obtain from it an up-to-date account of the main experimental findings and ideas of the past few years. Work on crystalline enzymes and on specific co-enzymes is justly given considerable prominence, the chapter on the proteolytic and related enzymes being a particularly useful one. On the other hand, references to the *synthetic* action of the intra-cellular "lytic" enzymes (which in the cell almost certainly preceded a synthetic $\rightleftharpoons$ hydrolytic equilibrium) are somewhat scanty. There is evidence in places of rather hasty writing and the use of occasional chemical slang ("This is the theoretical yield on maltose"; "obtained by washing yeast with H_2O"; "50 per cent. of the theoretical CO_2"; "until free of SO_4"), which will doubtless be removed in a second edition.

This book is strongly recommended to every chemist interested in enzymic processes, and to all students of biochemistry and physiology who require an up-to-date summary of recent investigations and ideas in this field. H. D. KAY

CHEMISTRY OF NATURAL PRODUCTS RELATED TO PHENANTHRENE. By L. F. FIESER. American Chemical Society Monograph Series, No. 70. Pp. xii + 456. New York: Reinhold Publishing Corporation. 1937. Price 35s.

The first edition of this book was reviewed in THE ANALYST last September, and the fact that another edition has been called for scarcely a year after its first appearance is a proof of its utility. The work has not been re-written, and corrections and minor changes have been effected in such a way that no alteration in pagination has been required. The extra 98 pages of the present edition result from the inclusion of an appendix of 90 pages in which the order of the main portion of the book is followed, whilst the index has been necessarily expanded to include the newer work. The author has endeavoured to include complete references to papers published up to January 1st, 1937, and he dates his preface from Cambridge, Mass., on February 1st. Owners of the first edition seem able to bring the work up to date by obtaining the appendix separately, and it is to be hoped that Professor Fieser will continue to issue extra numbers at frequent intervals until it is necessary to re-cast the book on a more extensive scale.

Meanwhile Harvard University pursues its way in enlarging our knowledge of the phenanthrene group, not merely by the production of new derivatives, but also by considerations of structure (p. 3 of both editions) and of reaction conditions. Thus Price has recently concluded (p. 339 of Appendix) that the formation of phenanthrene dibromide proceeds by a chain mechanism, whilst Fieser and Price have investigated the effects of substituents on the phenanthrene-bromine equilibrium.

The arrangement of material in the Appendix follows that of the major portion of the work; thus Chapter I deals with the reactions of phenanthrene and the formation and properties of derivatives. The references are full, and those relating to the morphine alkaloids are given for the pharmacology as well as the chemistry of these compounds. New work on resin acids (Chapter II) needs a short appendix, and the carcinogenic hydrocarbons (Chapter III) a longer one, owing to the intensive study of these compounds by Cook and his co-workers. The reviewer of the first edition applied the term *pivotal* to Chapter IV (sterols and bile acids); its appendix accounts for a further 25 pages, and those to Chapters V (sex hormones) and VI (heart poisons) add 26 and 21 pages, respectively. Points in these chapters are the possible necessity of revision of the formulae of the unsaturated acids derived from cholic acid, the relationships of ergosterol, calciferol and vitamin *D*, stereochemical nomenclature, toad poisons and other matters of probably equal importance. The use of surface-film measurements by Askew, Farmer and Kon as a control on accepted formulae (*e.g.* sarsasapogenin, p. 427) is an example of the use of a physical method which is finding other applications.

Professor Fieser has dealt with a complicated subject in a masterly and interesting manner, and is to be warmly congratulated on his book. The printing is excellent and the representations of constitutional formulae leave nothing to be desired; even methyl and ethyl groups are printed as they should be, and not as Me and Et.

J. T. HEWITT

SEPTEMBER, 1937 Vol. 62, No. 738

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Death

With great regret we record the death, on July 26th, of William Jefferys Lesley, who had been a member of the Society since 1930.

Flour Spoilage

By D. W. KENT-JONES, Ph.D., B.Sc., F.I.C.

(Read at the Meeting of the North of England Section, April 10, 1937)

Introduction.—When the chemist who specialises in the examination of flour is asked to make a report, it is usually with the object of assessing the value of a sample for the particular purpose for which it is intended, such as the making of bread under a specified fermentation system, or the manufacture of cakes, biscuits, and the like. It is well known that wheats of various origin, when milled, may give flours of very different qualities for breadmaking and so on, so that, although a flour may be quite sound and wholesome, it may not have the desired characteristics when made into a dough. The examination of flour for breadmaking has become a specialised matter, involving both chemical and physical tests, and the use of expensive dough-testing apparatus.

In this paper, however, I am not dealing with these specialised problems, but with general faults concerning the wholesomeness and palatability of the flour, which render it unsuitable for general use. I have attempted to consider these faults under the term "flour spoilage" and to give examples of the more common types. Fortunately they are comparatively rare, when we consider the large amount of flour produced.

Taints.—Flour particles are extremely small (being dressed through "silks" with meshes ranging from 100 to nearly 200 to the inch), and hence the surface is very great as compared with the volume. Owing to this fact flour will readily become tainted through the absorption of any odours in its vicinity and, although out-of-condition and unsatisfactory flour, or flour that has been spoiled, is not common, yet when this trouble does arise, it is generally due to the presence of taint. The taint, however, may not have been acquired subsequent to the making of the flour, but may be due to the fact that the wheat from which the flour was made was tainted and unsatisfactory. The commonest of these taints is probably "mustiness," and "mustiness" may certainly be due to the wheat itself being out of condition when it was ground into flour. English wheat that has been stored for a long time under unsatisfactory conditions may impart a musty taint to the flour. For example, if the wheat is kept from harvest until the spring of the following year, it sometimes develops "must," which taints the flour. "Out-of-condition" English wheat is not rare in the spring, but as a rule it is noticed and not ground into flour. "Mustiness" is often associated with a high mould count, but there has not been, to the best of my knowledge, sufficient work done for a dogmatic statement to be made on this point, for undoubtedly there have been musty flours with low mould counts. Whether or not such flours have once had a high mould count cannot be ascertained. Normally, however, the mould-content of flour tends to increase on storage, whilst bacterial contamination usually decreases.

All wheat contains foreign seeds, which are normally extracted in the cleaning process preparatory to milling, but sometimes they escape and are ground up in the flour. Most of them are harmless, but some will cause taint. A well-known example is the seed of *Melilotus*, which gives a sweet, hay-like flavour to the flour, and failure to eliminate this has caused serious trouble in the past. The *Melilotus* seed, which is very small and brownish-yellow, is often present in wheat from Russia and the Argentine. If *Melilotus*, of which there are several varieties, is present in wheats grown in hot countries, it is less likely than the *Melilotus* from temperate climates to cause taint. When wheats contaminated with these seeds are used, great care in cleaning is necessary, and the wheats must not be warmed or damped, as is done in the conditioning process preparatory to milling, until these seeds are removed, or the taint may become diffused and so be absorbed by the grain itself.

Other taints sometimes encountered are the odours of apples, oranges, phenols, and so on, which have been acquired during transit. For instance, I have known flour sent from Australia acquire the odour of apples, owing to its being loaded in a ship containing also a consignment of Tasmanian apples. Almost any taint may be acquired in this way, and the variety is at times startling. The odour of eucalyptus, due to the presence of eucalyptus leaves in the wheat, is occasionally encountered, especially in Australian flour.

Sometimes wheat becomes hot on storage and the grains have an incipient charred appearance. They are termed "bin burnt," and such grains often have a distinctive hot taste. This may result in the flour, subsequently milled from it, having a dull colour and the same unpleasant flavour. Wheats that heat in the stack are the usual cause of "bin burnt" grains.

It is not always appreciated that the baker is likely to experience trouble with tainted flour, even when the analyst may think the taint is almost too slight to worry about. It is distinctly difficult to test for taint in flours that are only slightly affected. The best way, of course, is the simple procedure of making the flour into a smooth paste with cold water and scalding by the addition of boiling water. A sensitive nose, however, is required. The baker has a much more effective test. As soon as he opens the door of his oven after baking, volumes of steam roll out and, if there is any taint in the flour, it is perceptible in the steam from the bread and is very pronounced. In other words, the test that we apply is the same test as the baker's, but it is made in a very much less effective manner.

OTHER POSSIBLE DEFECTS DUE TO STORAGE.—Difficulties connected with the moisture-content of the flour may arise, but it is outside the scope of this paper to deal with loss of weight in storage (usually only of importance in small bags of self-raising flour) which is dependent on the vapour pressure of the flour and the relative humidity of the air in which it is stored.

On the other hand, if a flour has a high moisture-content and it is stored under pressure, as, for instance, when bags are piled up on top of one another, and particularly if the temperature is warm, as in the hold of a ship, hard lumps may form. This phenomenon is connected with the "respiration" of the flour. Such flour becomes completely unsatisfactory for ordinary purposes, and I have seen lumps fully a foot in diameter taken out of bags. Some bags set almost like cement. This is due to the flour having too high a moisture-content and being stored under the unfavourable conditions I have indicated. If such flour is reground and dressed, and provided that any lumps that contain discoloured pieces are discarded, it is often possible to re-mix it in small proportions with normal flour.

Sometimes flour becomes markedly acid on prolonged storage, but only if there are unfavourable conditions, such as excessive warmth and high moisture-content. Rancidity is also known, but is comparatively rare.

Damage due to sea water is, of course, well known, and I would draw special attention to the paper on the subject by Seaber (ANALYST, 1936, **61**, 14).

PESTS.—Troubles due to actual pests are also rare and are more common with wheat than with flour. The main trouble in this respect is due to the flour mite (*Acarus farinae*), and this, again, is more prevalent when the flour has a high moisture-content and has been stored in a warm place. No flour is sterile as regards either bacteria or insect eggs and, if the conditions are favourable, the latter will hatch and the insects multiply unduly. The appearance of the flour mite under the microscope is well known. Flour badly infested with mites becomes almost purple in colour, owing to the presence of thousands of mites and, if the flour is flattened with a spatula, the surface rapidly becomes uneven and rough as the result of the movements of the insects. Such flour, of course, cannot be used for normal purposes and has usually to be thrown away, although it is sometimes mixed with offals. This practice may also cause trouble.

The Mediterranean flour moth is a troublesome pest in the mill, but is only rarely met with in the finished flours. It is conceivable, however, that, if there were a burst in a "silk," one might find in the flour a matted mass of caterpillar silk. The moth lays its eggs in crevices, and the caterpillars are hatched in four to fourteen days. These caterpillars spin large quantities of a silk which becomes encrusted with the flour dust, and these masses may choke the mill. The duration of the caterpillar stage may be several months. The moth causes sufficient trouble to make it necessary to fumigate mills with hydrogen cyanide, ethylene oxide or the like.

I have known mills to be infested with *Niptus hololeucus*, cadelle, *Tribolium confusum*, and mill worm, and there is always the danger of contamination of flour with rat and mice droppings. The fact that the flour is sifted through silks before being sacked generally means that, if such extraneous matters are found, the flour has become contaminated after leaving the mill. If flour has been badly contaminated with rat or mice dung it is, of course, likely to have a high bacterial population and particularly a high *B. coli* and *B. perfringens* count.

Attention should also be drawn to possible damage by the wheat bug (*blé punaise* or *Weizenwanze*); this seems to be mainly restricted to Central Europe, Persia, Syria and Morocco. There are a number of such wheat bugs, but the principal ones are *Eurygaster maurus*, *E. intriceps*, *Aelia rostrata* and *A. acuminata*. Grain thus damaged has a minute puncture surrounded by a yellow patch. Although the bug itself is seldom, if ever, met with in flour, the result of its attack is that the flour acquires excessive proteolytic activity, so that, when made into a dough, it becomes sticky and often unusable. The presence of only three per cent. of infected wheat can cause very serious damage. The examination of flour for this damage requires expert knowledge and is often carried out with the aid of special dough-testing apparatus, operating on fermenting doughs. If, however, the gluten from infected flour is washed out and allowed to stand under water for 1 to 2 hours, it shows a great tendency to "run," and loses its elasticity.

OTHER TYPES OF FLOUR SPOILAGE.—I have not attempted to deal with every possible type of flour spoilage. There might, for example, be trouble from the presence of ergot in flour, if the wheat from which it is made contains a sufficient quantity of the parasite and this has not been removed in the cleaning process. This is so rare in England and, indeed in most countries, that I have never had an example sufficiently pronounced to cause any trouble or difficulty, but the possibility always exists (*cf.* Barger, ANALYST, 1937, 352).

Trouble also arises sometimes from coloured spots in bread, and it is claimed that this may be due to discoloration in the flour. Numerous suggestions have been made to account for this, such as the presence of cow wheat (*Melampyrum arvense* L.), which, when ground, is said to yield a blue mass, the presence of blue stones, etc., but in practically every case the trouble is due to the presence of copying-ink pencil. A pencil may have been dropped into the wheat in milling, and have become powdered by the rolls, or a copying-ink pencil may have been sharpened in proximity to the stored flour and the minute particles thus produced have been picked up by the sack. If the former happens, the silks naturally do not sift out the minute specks and, when the flour is wetted for dough, the methyl violet spots spread and stand out. They can be seen in the dough and bread, and are easily identified. The stain dissolves readily in alcohol, and a low-power microscope usually reveals the presence of particles of graphite. The stain can be absorbed on a filter-paper, and the dyestuff may be identified by adding reagents such as potassium nitrite in dilute acetic acid (which changes the colour from violet to blue) or stannous chloride in hydrochloric acid, which turns the violet to green.

"Rope" is a disease which may develop in bread on storage. In the first place the bread develops yellowish-brown, slightly sticky, spots. At the outset the odour is only reminiscent of slightly over-ripe fruit, but it gradually becomes worse, and may sometimes be extremely repugnant, while the loaf itself may become a putrefying mass. The disease is due to the presence of bacteria of the *Mesentericus* group, mainly *Mesentericus vulgatus*. These are spore-forming organisms, and the spores are always present even in the best and purest flour. Provided, however, that their number is not excessive and that the conditions of bread storage are normal, the bacteria are not likely to multiply and, hence, the trouble will not arise. The spores, of course, resist the heat of the oven and, if the bread is stored under warm and moist conditions, and particularly if the yeast fermentation has been slow and sluggish, the trouble may develop. The spores then turn into the vegetative forms and rapidly multiply. At one time it was thought that the trouble was mainly due to flour that was too "ropy" or to lack of cleanliness in the bakehouse. While both these causes may aggravate the trouble, outbreaks arise only when bread is stored in a warm condition for too long periods, and then only if the bread has been made with a rather slow and insufficiently vigorous fermentation. If ropy bread appears it should, of course, be immediately destroyed and every precaution taken to prevent the bacteria from multiplying. Fortunately, *Mesentericus vulgatus* cannot exist in an acid medium, and it is therefore helpful to wash out all the troughs and other vessels with acid, such as vinegar, and even to incorporate acid substances, such as vinegar or acid calcium phosphate, in the succeeding doughs. Above all, the bread must be rapidly cooled, as then no difficulty is likely to arise. Hence, one-pound loaves, which cool more rapidly than four-pound loaves, may escape the trouble, whilst the larger ones are affected. Loaves should not be heaped together so that they cool slowly, and wrapping before cooling is also bad practice. The trouble, of course, comes only in hot weather. In warm climates there is often serious trouble from rope, which in England is rare. Practically all bread, especially if fermentation has not been vigorous, will develop rope on storage under conditions of warmth. I should like to emphasise the fact (*cf.* Amos and Kent-Jones, ANALYST, 1931, **56**, 572) that if the dough is made with a vigorous yeast fermentation, there is always less likelihood of trouble arising than if the fermentation is slow and sluggish. As a matter of fact, it is difficult to cause rope to develop to a pronounced extent in bread made with cool doughs and plenty of yeast.

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The Volumetric Determination of Mercury

By M. FITZGIBBON, A.I.C.

The work here described was undertaken to ascertain the most suitable method for determining mercury in organic compounds or in mixtures such as seed-disinfecting preparations.

A brief survey of well-known procedures for determining mercury shows that they may be classified as follows:—

(1) Reduction to mercurous chloride and separation of that salt prior to the final titration.

(2) Reduction to the metallic state.

(3) Direct method with potassium iodide in neutral mercuric salt solution.

(4) Acidimetric method, based upon the non-ionisation of mercuric cyanide.

(5) Determination with thiocyanate, directly in mercuric salt solutions or indirectly, as a zinc complex, involving separation and subsequent titration with iodate in strongly acid solution.

Of these methods, Nos. 1, 4 and 5 may be ruled out as unsuitable on account of being too tedious; method No. 3 can be used only with a neutral and pure solution of mercuric chloride; No. 5 is unreliable in the presence of chlorine or nitrogen oxides. The remaining procedure (No. 2), due to Rupp,[1] whilst excellent in theory, is liable to yield wholly unsatisfactory results, owing to some of the metal not reacting after the addition of iodine; this is due to the tendency of the reduced mercury to aggregate.

The addition of gelatin has the remarkable effect of retaining the reduced mercury in a stable "colloidal" suspension—in fact, so reactive is the metal in this state that it is almost possible to titrate directly with iodine, instead of adding an excess and back-titrating with thiosulphate. The presence of large amounts of alkali sulphate, chloride or nitrate has no influence upon the physical condition of the mercury, and interference by most substances, except such obvious ones as cupric salts (reduced by formaldehyde) and substances capable of being oxidised by iodine in acetic acid solution, need not be anticipated. The presence of cyanide does not affect the determination, and the procedure is, therefore, suitable for mercuric cyanide.

The improved method is as follows:—The mercuric solution resulting from the destruction of the organic mercurial preparation by any of the methods suggested below, is passed through a Gooch filter if there is any considerable quantity of insoluble matter (talc and silicious residues, present as "carriers" in seed-dressing compositions, remain after the preparation has been treated with sulphuric acid). The filtrate is treated with sufficient potassium iodide (about 1 g.) to form the soluble double salt, and then rendered alkaline with 5 *N* sodium hydroxide solution (an excess of about 5 ml. being added), and heated to about 60° C. Two ml. of freshly prepared, warm 2·5 per cent. gelatin solution are added, and then, with constant swirling, 3 to 4 ml. of 40 per cent. formaldehyde solution.

Reduction is extremely rapid, and the solution assumes a sepia shade, which may not be quite so dark if less gelatin is employed; in the absence of the colloid the colour is grey. The reduced mixture is cooled to about 20° C., acidified with excess of acetic acid, treated at once with 25 ml. of $N/10$ iodine solution and stirred, and the excess of iodine is titrated with $N/10$ thiosulphate solution (1 ml. of $N/10$ iodine $\equiv$ 0·01003 g. of mercury).

The satisfactory working of this procedure depends to some extent upon the method of preparing the mercury solution; the following notes on this point will be found of assistance:—Simple aliphatic mercury halides such as the higher alkyl (*e.g.* propyl) mercury chlorides, ethanol mercuri-chloride and the like, readily decompose when heated with conc. sulphuric acid, yielding mercuric sulphate; since some sulphur dioxide is produced by the action of the acid upon the alcohol or carbon residue of the compound, the solution and washings must be oxidised. Addition of bromine water, with subsequent boiling to remove the excess, is a satisfactory method of oxidation and ensures that all the mercury is in the mercuric state. Readily volatile and stable alkyl compounds are more safely decomposed by making them react with pure bromine in a pear-shaped flask fitted with a ground-glass air condenser. The resulting mixture of mercuric bromide and brominated compounds is heated with sulphuric acid in the usual manner, care being taken to avoid loss of mercury by sublimation.

Heating aromatic compounds with sulphuric acid usually leads to considerable charring, and prolonged heating at high temperature is necessary before the solution becomes colourless. The addition of a few drops of conc. nitric acid, however, to the dark sulphuric acid solution effects rapid clearing.

The sulphuric acid solutions, after short and rapid boiling, are ready for the addition of potassium iodide prior to reduction in alkaline solution.

The following results are typical of those obtained with this modification of Rupp's method:

Mercuric Chloride.—The 25 ml. of solution taken was calculated to contain 0·1252 g. of mercury. The gravimetric determination gave 0·1244 g. and the volumetric method 0·1238 g. of mercury (= 99·52 per cent. of the gravimetric result).

Ethyl Mercuric Chloride.—The salt was purified by recrystallisation from alcohol, and quantities of (1) 0·303 g. and (2) 0·2014 g. were used for the determination. As the C–Hg linkage in this compound is remarkably stable, the following procedure was followed:

The weighed sample was transferred to a pear-shaped 200-ml. saponification flask fitted with a ground-glass air-condenser about 30 cm. long. Two ml. of conc. sulphuric acid were pipetted down the condenser and then 1 ml. of anhydrous bromine. The reaction was completed by carefully heating the flask over a Bunsen flame. After cooling, about 25 ml. of water were poured down the condenser, and heating was continued until the bromine had almost ceased to appear as drops in the tube. The liquid, which was still yellow, was washed into a 250-ml. beaker, made up to about 125 ml., and boiled until free from bromine, a few grains of silver sand being added and the beaker covered with a clock-glass. After cooling, excess of potassium iodide was added; this caused liberation of a trace of free iodine, which was removed by adding a drop or two of thiosulphate solution. The liquid was then rendered alkaline with soda and treated as described above. The amounts of mercury found were (1) 75·14 (2) 75·70 per cent. Theory, 75·67.

It would appear that for compounds of this type a tolerance of ±0·50 per cent. of mercury must be allowed; a variation of 0·10 ml. in a titration in the second determination introduced an error of this order. With care, however, and if a 25-ml. burette graduated to 0·05 ml. is used, consistent results of a high order of accuracy should be obtained.

Commercial Seed Dressings.—The proprietary article examined was "Semesan," stated to contain 30 per cent. of hydroxymercuri-chlorophenol.

The sample was prepared for reduction as follows:—One g. was treated with 4 ml. of conc. sulphuric acid in the apparatus described above, the flask being rotated to ensure thorough mixing. The pasty, dark coloured mass was heated fairly strongly, during which process some mercury sulphate sublimed and collected upon the cooler parts of the flask. After cooling, 1 ml. of conc. nitric acid was added, and the flask was gently heated; this caused the liquid to be appreciably decolorised. About 15 ml. of water and a few drops of bromine were then introduced, to ensure complete oxidation of the mercury and to saturate any trace of organic nitro compounds which would otherwise absorb iodine. The mixture was heated to boiling for a few minutes, then cooled and diluted somewhat, before being transferred to the 250-ml. beaker and treated as described above. Owing to the higher salt-content, some of the gelatin separated in flocculent clots, but this did not prevent the mercury from being finely dispersed and reacting quantitatively with the iodine (*vide infra*). The amount of mercury found was 17·15 per cent., compared with 17·40 per cent. calculated to be present.

Application of a drop of sulphuric acid to the ground-glass surface of the reflux tube prevents troublesome "binding" due to mercury sublimates at the joint; washing of this part is also facilitated. If, owing to variations in the salt concentration of the solutions, the gelatin clots and adsorbs mercury as a precipitate, it is useless to continue the determination; this is unlikely to occur, however, if care is taken and, moreover, is readily observed.

I wish to express my thanks to Dr. A. M. Ward, of the Municipal College, Portsmouth, for examining the method.

REFERENCE

1. E. Rupp, *Ber.*, 1906, **39**, 3702; Abst., ANALYST, 1906, **32**, 128.

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The Colorimetric Determination of Copper with Sodium Diethyldithiocarbamate in the Presence of Moderate Amounts of Iron

By T. P. HOAR, M.A., Ph.D., B.Sc.

The colorimetric determination of copper by means of the yellow compound formed with sodium diethyldithiocarbamate is described by Callan and Henderson,[1] who suggest the removal of interfering iron by precipitation as ferric hydroxide with ammonia. However, as shown by Toporescu,[2] Haddock and Evers[3] and Hammence,[4] some copper is carried down by the ferric hydroxide even under the best conditions. To avoid this error, Haddock and Evers[3] add citric acid and ammonia to the solution containing copper and ferric iron. Sodium diethyldithiocarbamate solution is then added; the iron does not react under these conditions, and the yellow compound formed with the copper is extracted with four portions of carbon tetrachloride, as suggested by Grendel.[5] In this way copper may be determined in the presence of 50,000 times as much iron by weight. McFarlane,[6] following Warburg[7] and Drabkin and Waggoner,[8] prevents the reaction of iron (up to 90 times the amount of copper) by the use of an ammoniacal pyrophosphate solution, and extracts the copper compound with amyl alcohol; according to Thatcher,[9] isoamyl alcohol is better.

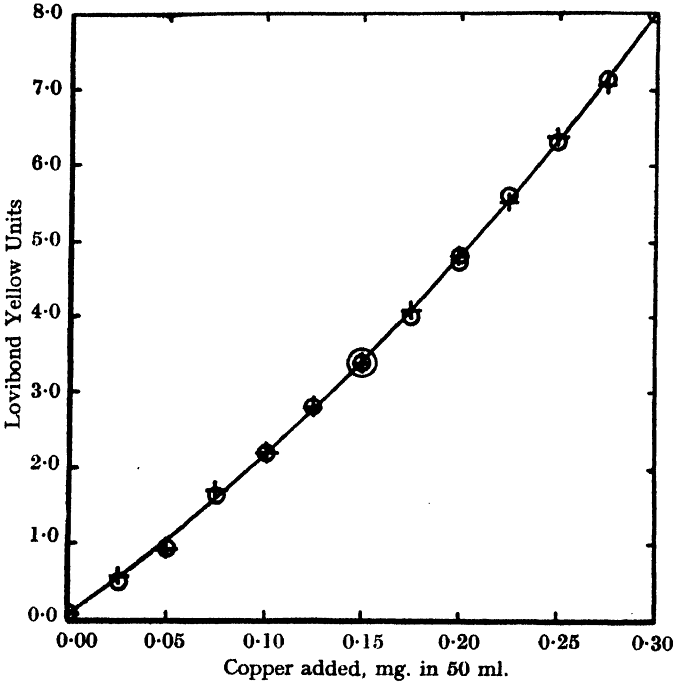
These extraction processes serve a dual purpose. First, the copper compound with sodium diethyldithiocarbamate is very sparingly soluble in water, all but the palest yellow solutions soon becoming cloudy and unsuitable for colorimetry, whereas it is readily soluble in organic solvents, giving suitable clear solutions; however, clear aqueous solutions may be obtained by the addition of a protective colloid, gelatin or gum tragacanth being recommended by Moseley, Rohwer and Moore.[10] Secondly, the yellow colour is separated from that due to ferric salts in the aqueous phase.

Since effective extraction may be very tedious, two methods of avoiding it when the iron present does not exceed about 100 times the amount of copper—a condition frequently encountered in practice—have now been devised. The first method is suitable for the determination of copper in the presence of some 25 times as much iron and a considerable amount of zinc. The second is suitable for larger amounts of iron, but is interfered with by zinc.

In the first method the iron is prevented from reacting with the sodium diethyldithiocarbamate by the addition of citric acid and ammonia, as in the procedure of Haddock and Evers.[3] A small amount of gum arabic is added and, on addition of the thiocarbamate, a clear golden-brown colour, excellently stabilised by the protective colloid, is obtained. The total yellow constituent of the colour is measured directly in a Lovibond tintometer. Any yellow colour due to ferric iron in the ammoniacal citrate solution is measured separately in another portion of the solution, to which all the reagents except the sodium diethyldithiocarbamate have been added. Subtraction of this small value from the total yellow colour value gives that due to the copper compound.

In the second method the iron is prevented from reacting by the addition of sodium pyrophosphate, as in the procedure of McFarlane,[6] but no ammonia is added; no yellow colour due to ferric iron then appears, and the colour subtraction process is unnecessary. Gum arabic and sodium diethyldithiocarbamate are added, and the yellow constituent of the aqueous solution is measured; exactly the same copper colour is produced as in the first procedure.

CITRATE METHOD.—*Solutions required.*—(1) Citric acid solution, 200 g. per litre; (2) ammonia, 100 g. per litre (1 vol. of ammonia of sp.gr. 0·880 to 2 vols. of water); (3) 1 per cent. gum arabic solution, prepared according to the directions of Zinzadze,[11] by dissolving at 50° C., cooling and adding 1 ml. of toluene per litre; (4) 0·2 per cent. sodium diethyldithiocarbamate solution. All reagents should be as free from copper as possible; the water should be condensed on silica or pyrex.



Standardisation Curve of Tintometer

Fig. 1

Procedure.—Place a 10- or 20-ml. aliquot portion of a suitably diluted solution (0·005 to 0·025 mg. of copper per ml.), containing any iron in the ferric state, in a 50-ml. flask. Add 10 ml. of citric acid solution (1), 8 ml. of ammonia (2) and 5 ml. of gum arabic solution (3), well mix, add 5 ml. of 0·2 per cent. sodium diethyldithiocarbamate solution (4), and make up to 50 ml. Measure the colour in a 1-cm. cell in a Lovibond tintometer, reading yellow units and using red and neutral tint for matching the tints only; this colour may conveniently be between 2·5 and 6·5 yellow units. Repeat with another 10- or 20-ml. aliquot portion, omitting the sodium diethyldithiocarbamate solution; this colour should not exceed 0·6 yellow units. Obtain the yellow units due to the copper by subtraction and thence the copper from a standardisation curve such as that shown in Fig. 1. The circles represent points obtained by this method from copper solutions of known concentration.

Where rapidity is essential but the greatest accuracy is not required, the iron colour and the total colour may be measured consecutively in the same aliquot portion; the iron colour, without the copper reagent, is first measured, and then the total colour by adding 1 drop of a 2 per cent. solution of the reagent direct to the 1-cm. cell.

It is advisable to standardise any particular tintometer against copper standards containing all the reagents, to allow for local variations in lighting, and so on; the standard curve once obtained (*cf.* Fig. 1) automatically eliminates all blank corrections. Alternatively, the following table, obtained from the smoothed curve of Fig. 1, may be used to construct a large-scale curve, but the appropriate blank correction must be found for the reagents used.

TABLE I

Lovibond yellow units		Copper present mg. per 50 ml.
1·0		0·052
2·0		0·098
3·0	with 0·1 neutral tint	0·139
4·0		0·177
5·0		0·211
6·0		0·244
7·0		0·275
8·0		0·304

Since the copper colour is a more reddish yellow than the iron, it is necessary to employ a colorimetric system, such as that of the tintometer, by which the amount of (arbitrary) yellow in each colour may be measured.

Test of the Method.—It was necessary to show that the colours produced by copper with sodium diethyldithiocarbamate and by ferric iron in ammoniacal citrate solution do not interfere with each other, and that ferric iron itself forms no colour with the reagent under these conditions. The effect of excess of nitrate, which may be present owing to its use in oxidising the iron or for other reasons, was also investigated. Various amounts of copper with different amounts of copper-free ferric iron (prepared from carbonyl iron) and potassium nitrate were taken in a total volume of 50 ml.; and the copper was determined by the colour subtraction procedure by an operator to whom the composition of the solutions was unknown. The results, in order of experiment, were:

Copper taken mg.	Iron taken mg.	Nitrate taken mg. NO_3'	Copper found mg.
0·26	2·3	46·5	0·27
0·62	1·6	25·5	0·62
0·38	0·0	87·0	0·37
0·21	0·8	64·0	0·20
0·84	0·4	17·5	0·83
0·50	0·5	0·0	0·51
0·40	10·0	0·0	0·39
0·25	2·5	2500	0·25

Evidently the colour subtraction procedure is valid, and a great excess of nitrate does not interfere. Haddock and Evers[3] mention that nitrate up to 0·75 mg. NO_3' in 50 ml. is permissible with their method; the present results indicate that far more may be tolerated.

Any nitrite present should be removed by making the original solution slightly acid with nitric acid, adding 0·5 g. of urea, and boiling the mixture for a short time.

Zinc, if present in large excess, may give rise to a turbidity; this can be prevented by making the solution more strongly ammoniacal, as in the original method of Callan and Henderson.[1] Arsenate does not interfere. As regards other interfering substances, the work of Haddock and Evers[3] should be consulted.

The copper colour is stable for at least 8 hours.

PYROPHOSPHATE METHOD.—*Solutions required.*—(1) Sodium pyrophosphate solution, 40 g. per litre of $Na_4P_2O_7$ dissolved in cold water; (2) 1 per cent. gum arabic solution; (3) 0·2 per cent. sodium diethyldithiocarbamate solution.

Procedure.—Place 10 or 20 ml. of the nearly neutral solution containing copper (0·005 to 0·025 mg. of copper per ml.) in a 50-ml. flask. Add 10 ml. of sodium pyrophosphate solution (1) and 5 ml. of gum arabic solution (2), well mix, add 5 ml. of sodium diethyldithiocarbamate solution (3), and make up to 50 ml. Measure the yellow units of the colour in a 1-cm. cell in a Lovibond tintometer. Read off the copper from a standardisation curve such as that shown in Fig. 1. The crosses represent points obtained from known copper solutions by this method.

It may be noted that the standard points obtained by the pyrophosphate method fall on exactly the same curve as those obtained by the citrate method for the reagents used in this work. It is best to construct a standardisation curve for any particular tintometer and reagents, or Table I may be used as before.

Since no colour subtraction is involved, any form of colorimeter is suitable. More dilute solutions (down to 0·0002 mg. of copper per ml.) can be dealt with by using a long tube of the coloured liquid.

Test of the Method.—Various solutions containing copper, ferric iron and nitrate were analysed, their composition being unknown to the operator. The results, in order of experiment, were:

Copper taken mg.	Iron taken mg.	Nitrate taken mg. NO_3'	Copper found mg.
0·58	10·0	0	0·59
0·40	7·5	55	0·39
0·32	12·0	0	0·33
0·38	10·0	500	0·38
0·90	0·0	250	0·88
0·60	5·0	100	0·60

Zinc gives a turbidity which can be avoided only by making the solution strongly ammoniacal; this gives a deeper colour due to ferric iron than that obtained by the citrate method, which is therefore to be preferred when zinc is present. Arsenate does not interfere.

The copper colour is stable for at least 8 hours. Very little change was observed after one day in a solution kept in a stoppered bottle.

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THE METALLURGICAL LABORATORIES
UNIVERSITY OF CAMBRIDGE

The Colorimetric Determination of Tin by Means of Toluene-3:4-dithiol ("Dithiol")

BY R. E. D. CLARK, M.A., PH.D.

IN a previous paper[1] I have shown that substituted benzene-1:2-dithiols are very delicate and highly specific reagents for tin, and that after addition of thioglycollic acid the test is independent of the initial state of oxidation of the metal. Details have also been given of a method by means of which tin can be roughly estimated with 4-chlorobenzene-1:2-dithiol.

The comparative difficulty associated with the preparation of the 4-chloro-compound, together with the fact that toluene-3 : 4-dithiol is now available commercially ("dithiol"), indicated the necessity for using the latter compound whenever possible. Accordingly a technique has now been worked out by means of which accurate colorimetric determinations of tin may be made with this derivative.

THE REAGENT.—"Dithiol" (0·2 g.) is dissolved in 100 ml. of 1 per cent. sodium hydroxide solution, and 0·3 to 0·5 g. of thioglycollic acid is added. The reagent thus prepared is stable for a considerable time, and there is no need to keep the solution in an atmosphere of hydrogen. If at any time a milky white suspension of the disulphide is formed, the reagent should be discarded.

METHOD.—If a solution containing tin is heated after addition of the "dithiol" reagent, the red precipitate rapidly coagulates and accurate colorimetric work is rendered impossible. Coagulation can, however, be stopped by the addition of agar-agar, as suggested by Dr. T. P. Hoar.

For the determination of tin the acid solution containing the metal is treated with thioglycollic acid (a few drops per litre) to ensure reduction to the stannous state and is then diluted until it contains not more than 60 p.p.m. of tin. A measured quantity (5 ml.) of this solution is placed in a graduated test-tube, and 1 ml. of conc. hydrochloric acid and 1 ml. of a warm jelly of agar-agar are added. The solution is then carefully heated to boiling and maintained at that temperature for a few seconds until the whole of the agar-agar is in solution. It is immaterial whether the tin-containing solution is added before or after the boiling of the solution, but unless the agar is completely dissolved the final colour fluctuates and reproducible results cannot be obtained. The tube is then cooled under the tap, and 2 ml. of the reagent, together with sufficient water to bring the total volume to 10 ml., are added. Finally, the tube is immersed in a boiling water-bath for 60 seconds, after which the liquid is ready for colour measurement.

Measurement of the Colour.—Attempts to measure the colour by transmitted light showed that matching was difficult, the red colour being associated with a large proportion of yellow. As in the previous work, satisfactory results were obtained by the use of reflected light.

For this purpose a Lovibond tintometer, British Drug Houses pattern, was tipped up on its back edge, so that the tray lay in a horizontal plane, as shown in Fig. 1. A standard porcelain tray (3·3 × 3·3 cm.) was placed in position, and 2·0 ml. of the hot liquid were at once removed from the test-tube (which had previously been taken from the water-bath), by means of a calibrated dropping pipette and placed in the tray, giving a depth of liquid of almost exactly 2·0 mm. after cooling. The colour was then matched against the standard tinted slides.

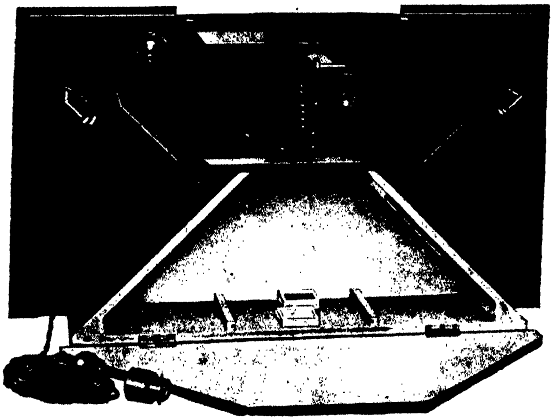

Fig. 1

For purposes of measurement the red units only were considered as significant, although it was always necessary to introduce a small amount of yellow into the matching colour, and occasionally a neutral tint, to adjust the brightness. It was found that the colour did not alter by more than 0·1 unit on standing for ten minutes, provided that the agar-agar was properly dissolved. Whenever alterations greater than this occurred, the results were ignored. In every instance the measurements could be repeated to within 0·2 red unit, and nearly always within 0·1 red unit over the range of concentrations of tin examined, that is to say, the accuracy of colour measurement was not less than that with which other variables were reproduced.

The figures obtained for a series of tin solutions of various concentrations are reproduced on p. 663, and in Fig. 2 the red units have been plotted against the tin-content in parts per million. It will be seen that a smooth curve is obtained for concentrations of tin up to 30 p.p.m. Beyond this point, however, irregularities occur, although it was found that individual readings were always repeatable. From these results it appears that, for measurements of the highest attainable accuracy, a tin concentration above 30 p.p.m. is inadvisable.

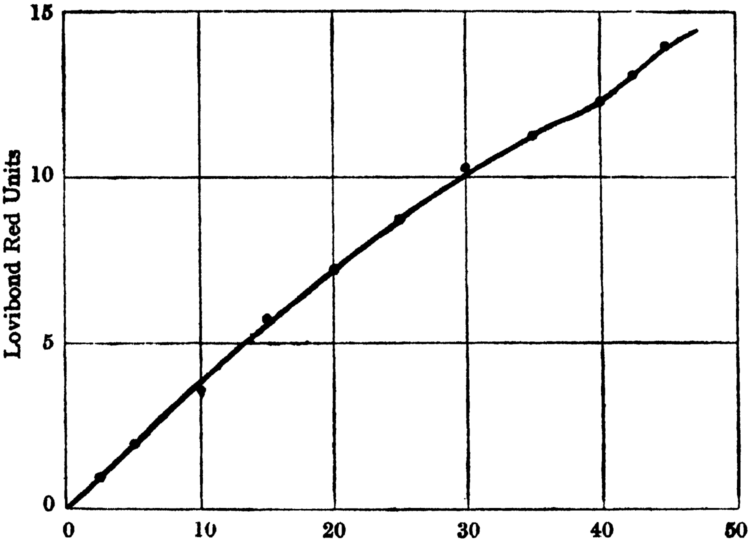

Fig. 2

Tin p.p.m. after dilution to 10 ml.	Colour (five minutes after removal from water-bath)		
	Red units	Yellow units*	Brightness* (Neutral units)
2·5	1·0	0·4	0
5	2·0	0·7	0
10	3·6	0·9	0·1
15	5·7	0·9	0
20	7·2	0·7	0
25	8·7	1·2	0·1
30	10·2	0·9	0·1
35	11·2	0·6	0·1
40	12·3	1·0	0
42·5	13·1	0·9	0·1
45	14·0	1·0	0
50	14·9	1·0	0·2

* Considerable variations were sometimes observed.

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UNIVERSITY CHEMICAL LABORATORY
CAMBRIDGE

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE OCCURRENCE OF COPPER IN PRESERVED PEEL (CITRON, ORANGE AND LEMON) AND IN GLACÉ CHERRIES

DURING the past few months I have experienced great difficulty in obtaining samples of the above-mentioned products (sugared or syruped) entirely free from copper. The amounts varied from 10 to 28 parts per million. Although, as a rule, the contamination is apparently due to the use of copper utensils during the manufacturing process, the matter is of importance, in view of the fact that copper colouring matter is prohibited by the Public Health (Preservatives, Etc., in Food) Regulations, 1925. Most of the determinations were made colorimetrically by several different methods, but in every instance both the dithio-oxamide and the sodium diethyldithiocarbamate reagents were used, the sample being prepared by the usual wet oxidation process with nitric and sulphuric acids.

EDWIN H. BUNCE

118, QUEEN'S GATE
SOUTH KENSINGTON, S.W.7.

TITRATION OF CARBONATES

WHEN carbonate is titrated with a dilute acid the indicator gives the "acid" colour, and after a brief pause returns to the "alkaline" colour; this occurs when the bicarbonate stage has been reached and continues until all the carbonate is in the form of hydrogen carbonate, when the indicator remains permanently at the "acid" colour. This phenomenon was first noted by Thiel, who published papers in the *Berichte* in 1913 (see also McBain, *J. Chem. Soc.*, 1912, p. 814, and Beckurt's *Die Methoden der Massanalyse*, 1931, p. 247); it is ascribed to the time taken to reach equilibrium $CO_2 + H_2O \rightleftharpoons H_2CO_3$.

It has been found here that the phenomenon is also well shown by the newer indicators, such as bromocresol purple and bromothymol blue, the colour change of which takes place between *p*H 5 and *p*H 8. On adding single drops of *N*/10 acid to *N*/100 sodium carbonate solution the period of delay is two or three seconds; on adding *N*/10 sodium hydroxide solution to *N*/100 carbonic acid solution the delay is longer—up to 15 or 20 seconds. Analogous results have been noted with dilute sulphurous acid and dilute ammonium hydroxide.

A. F. KITCHING

MONKTON COMBE SCHOOL
NEAR BATH

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF BRISTOL

REPORT OF THE PUBLIC ANALYST FOR 1936

OF the 1662 samples of food and drugs examined, 598 were formal and 1064 informal.

"MILK-O."—A sample sold under this fancy name gave the following analytical figures: Sp.gr., 1032·8; fat, 0·50; non-fatty solids, 8·55; ash, 0·65; chlorine in ash, 14·5 per cent.; Δ, 0·456°; starch present. It was probably made by boiling skimmed milk powder and starch with water. The cipher after the word "milk" is not supposed to be a measure of its value, but rather a ruse so that it does not come under the Sale of Milk Regulations, 1901 and 1912.

GROUND ALMONDS AND CASHEW NUTS.—The following results were obtained in the analysis of 9 samples of genuine ground almonds and 1 of ground cashew nuts, which are said to be a good and cheap substitute for ground almonds:

	Moisture Per Cent.	Ash Per Cent.	Oil Per Cent.	n_D^{40} of oil	Iodine value of oil
Ground almonds (mean of 9)	3·5	2·84	59·4	1·4632	96·3
Ground cashew nuts	3·7	2·55	30·0	1·4624	86·0

Two samples of ground almonds were adulterated with 10 and 4 per cent. of brown sugar, respectively.

MERCURIAL OINTMENT.—Five of 8 samples of weak mercury ointment contained about 10 per cent. of mercury, as required by the B.P. Codex, 1934; one contained about 15 per cent., and two were deficient in mercury (8·65 and 8·5 per cent.). One of these deficient samples, which had been purchased in a glazed cardboard box, was examined again after being 5 months in the laboratory, and was then found to contain 10·65 per cent. of mercury. Tests were therefore made with three samples of a mercurial ointment kept in different containers, and the following amounts of mercury were found:

Nature of container	Glazed cardboard Per Cent.	Wood-chip Per Cent.	China pot Per Cent.
Analysis made—			
1 day after purchase ..	9·7	9·6	9·6
3 weeks after purchase ..	11·1	10·1	9·6
5½ months after purchase ..	12·75	10·7	9·8

Thus it is useless to expect a correct determination of the mercury in an ointment of this type sold to the purchaser in a glazed cardboard box, unless the analysis is made within a day or two after the purchase.

AMMONIA IN SHRIMPS.—A tinned sample of shelled shrimps was examined, owing to exception having been taken by another authority to the presence of ammonia. The sample yielded 0·033 per cent. of ammonia on distillation with magnesium oxide, but it was not abnormal in this respect, since shelled fresh shrimps yielded 0·055 per cent. under the same conditions.

Feathers and Upholstery Material.—It is said that imported feathers are usually cleansed, but that home-produced feathers are often sold unwashed (*cf.* Analyst, 1928, **53**, 278; 1936, **61**, 252, 473). Tests were applied to 7 samples of feathers of unknown origin as follows:—Fifty g. were shaken at frequent intervals for 30 minutes in a large stoppered bottle with 1·5 litre of cold distilled water, the mixture was strained through a Buchner funnel, and the feathers were wrung out by pressure. The resulting effluent was filtered twice, and the soluble chlorine in the filtrate was determined gravimetrically. The oxygen absorbed in 4 hours from $N/80$ potassium permanganate solution at 27° C. was also determined.

In washing experiments, the original feathers were shaken for an hour with 3 litres of tap water, and the feathers were then wrung out by pressure and left for about a week on the floor of a sunny room. The moisture-content of the feathers before and after washing ranged from about 8 to 9 per cent. The effluent from the washed feathers was made in exactly the same way as the original effluent. Subsequently it was found that substantially the same chlorine figure was obtained by washing the 50 g. of feathers used for obtaining the original effluent, with 1·5 litre of cold tap water for an hour, wringing out with pressure, and filtering twice. The results obtained with the feathers and with various upholstery materials were as follows:

	Chlorine Parts per 100,000				Oxygen absorbed in 4 hrs. at 27° C. Parts per 100,000			
	Original effluent	After washing			Original effluent	After washing		
		1st	2nd	3rd		1st	2nd	3rd
Mixed featherdown	175	27	5	3	94	39	18	13
Poultry feathers	188	26	5	4	80	31	12	9
Duck feathers	160	39	13	—	47	34	12	—
Poultry feathers	15	13	—	—	30	26	—	—
Mixed poultry chopped feathers	45	16	—	—	90	42	—	—
Cheap mixed feathers	77	19	—	—	124	44	—	—
Duck feathers	145	47	20	—	150	46	20	—
Hair (new black)	8	—	—	—	13	—	—	—
Blackfield hair	18	—	—	—	19	—	—	—
Kapok	15	—	—	—	290	—	—	—
,,	56	—	—	—	489	—	—	—
Curled coconut fibre	56	—	—	—	111	—	—	—
New cotton waste	87	18	6	—	646	146	32	—
Millpuff	102	14	7	—	873	146	49	—
,, (white mixture)	27	—	—	—	541	—	—	—
,, (dark mixture)	40	—	—	—	258	—	—	—
Rag flock	35	10	6	—	202	61	28	—

These experiments show that it is quite practicable to wash feathers to conform with the standard of cleanliness prescribed for rag flock. F. E. Needs

METROPOLITAN BOROUGH OF HAMMERSMITH

Annual Report of the Public Analyst for the Year 1936

"Dairy Table Cream."—A sample sold under this name was found to consist of chocolate-flavoured blanc-mange powder, and contained no cream or milk powder; it was reported as adulterated.

WHITE MILK CHOCOLATE.—This was found to have been prepared from cocoa butter with milk and sugar (probably added as sweetened condensed milk), with no non-fatty cocoa solids. Cocoa butter is somewhat difficult to digest, and my information is that this so-called chocolate has not proved a success owing to its having caused biliousness in children. It was reported as adulterated.

F. W. EDWARDS

CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1936

MEASUREMENT OF SOLAR RADIATION.—*The Potassium Iodide Method.*—This process has been in continuous use for ten years. Although it suffers from several disadvantages (*cf.* ANALYST, 1927, **52**, 641; 1929, **54**, 101, 334; 1931, **56**, 314), the results are very consistent under standardised conditions. The figures for July, 1936, show a sudden drop, with a corresponding rise in August; this is almost certainly due to the heavy rainfall and resulting cloudy conditions in July.

The Nitrite Method.—This has been developed from the original work of Gillam and Morton (*J. Soc. Chem. Ind.*, 1927, **46**, 415; Abst., ANALYST, 1928, **53**, 60), who found that nitrite is developed by the action of ultra-violet light in an alkaline solution of potassium nitrate. In the modification adopted at Salford two parts of the same solution of alkaline nitrate are exposed side by side, one in a quartz tube and the other in a glass tube, and the difference in the amounts of nitrite formed is measured either by the Griess–Ilosvay method or the Riegler method. Although this nitrite can be formed only by ultra-violet light of wave-length below approximately $320m\mu$,* the curve of the results obtained shows a striking resemblance to that of the curve of the results obtained by the potassium iodide method; this would seem to indicate that the ultra-violet rays below $320m\mu$ vary in direct proportion to the total amount of solar radiation received.

Ashworth's Ultra-Violet Ray Meter.—The first type of this instrument (ANALYST, 1933, **58**, 690) has been superseded by one in which the paper wedge is replaced by varying thicknesses of wire gauze; this prevents any variation in the transmission factor due to dampness or to the discoloration of the wedge by sunlight. The transmission of the glass filter used is between 300 and $400m\mu$, with a maximum transmission of 80 per cent. at $360m\mu$. The wave-length of the rays of greatest medicinal value is of the order of $300m\mu$.

In my opinion, whilst the instrument will give definite information as to the total ultra-violet rays in solar radiation, yet, having regard to our knowledge of the extremely small amounts of ultra-violet rays of wave-length $300m\mu$ present, especially in winter sunshine, it cannot be assumed that a positive reading for ultra-violet rays with this instrument also indicates the presence of rays of therapeutic value.

The following table shows the relative intensities of ultra-violet light recorded at Salford and by a similar instrument at the Meteorological station at Southport:

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Regent Road, Salford	3·4	2·6	21	20	61	89	68	66	32	18	8	11
Hesketh Park, Southport	—	—	52	85	115	245	183	92	47	25	11	10

Integrating Solarimeter.—An instrument of this type, which is essentially a Moll pattern thermopile coupled with a sensitive milliampere-hour-indicator, was installed during the early part of the year. In this apparatus, which is calibrated by being exposed to a standard source of radiation, the solar radiation is transformed into, and recorded as electrical energy. The results are thus in terms of absolute units of energy and have a distinct advantage over those obtained by the other methods. The thermopile is non-selective and records total solar radiation, both visible and invisible. So far as I am aware, the only other instrument of this type in use is a recording solarimeter recently installed at the Meteorological Office, South Kensington. The following table gives the comparative figures, expressed in gram calories per sq. cm., for three months, obtained by the two instruments:

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* Ordinary glass bottles will transmit all rays longer than $320m\mu$; quartz transmits rays down to about $200m\mu$. Ultra-violet light from the sun is normally 300–$400m\mu$.

	Salford	South Kensington
September ..	99	188
October ..	53	110
November ..	12	42

ATMOSPHERIC SULPHUR POLLUTION.—Twenty-four monthly tests were made by the lead peroxide method (ANALYST, 1935, **60**, 122) and 253 tests at Regent Road by the volumetric sulphur method. In the former process sulphur pollution is returned as mg. of SO_3 per 100 sq. cm. of exposed surface, and in the latter the sulphur dioxide in the air is expressed as parts per million. Both processes show a very striking rise during the winter months, and the volumetric process (which enables daily determinations to be made) also shows very high results during foggy weather. The daily averages of sulphur dioxide in p.p.m. were as follows:

Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
0·070	0·094	0·075	0·073	0·073	0·047	0·042	0·039	0·037	0·033	0·093	0·071

G. H. WALKER

Department of Scientific and Industrial Research

WOOD PRESERVATIVES*

THE Report discusses the advantages and disadvantages of the various types of preservatives.

A. OIL TYPE PRESERVATIVES.—*Coal-tar Creosote.*—A brief account of the production and properties of various creosotes has been given by Richardson (*J. Brit. Wood Pres. Ass.*, 1934, **4**, 64). The British Standard Specification No. 144—1936 covers practically all the creosotes produced in this country and includes standard methods of test. Owing to the false idea that a good creosote must be black, it is difficult in practice to obtain creosoted wood of a light colour; black creosotes are invariably dirty.

Coal-tar.—This is less efficient as a preservative than the creosote derived from it, partly because it does not penetrate the wood so deeply. In admixture with creosote it is a satisfactory preservative for pressure treatment, but there is a tendency for the surface of the wood to be covered with a pitch coating which does not dry off.

Water-gas Tar Creosote.—Water-gas tar and its distillates have little or no toxicity for wood-destroying fungi, and their use should therefore be limited to diluting coal-tar creosotes. The distillates, sometimes offered as creosotes, are usually brown and are characterised by the lack of tar acids, a minimum content of which is demanded in all specifications for genuine coal-tar creosote.

Wood-tar Creosote.—Creosotes produced by the distillation of wood-tar are not prepared to any standard quality, and cannot compete in price with ordinary coal-tar creosote. They are good preservatives, but are said to be more corrosive than ordinary creosotes to metals. They are sometimes added to proprietary preservatives of coal-tar origin, particularly those intended to give the wood a warm, brown colour.

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* *Forest Products Research Records*, No. 17 (*Wood Preservation Series*, No. 3). By N. A. Richardson, B.Sc., A.I.C. H.M. Stationery Office, 1937. Price 6d. net.

Petroleum Oils.—In U.S.A. and India crude petroleum, "topped" petroleum and petroleum fuel oils are used in admixture with coal-tar creosote, particularly for the preservation of railway sleepers. In themselves they have little, if any, toxicity for wood-destroying fungi.

Waste Sump Oil.—Used by itself waste sump or crank-case oil is practically non-toxic to wood-destroying fungi, although it might be used as a solvent for an oil-soluble toxic material. Tetrachlorophenol has been suggested as a suitable chemical to dissolve in the oil.

B. Water-soluble Type Preservatives.—Recent developments in this type of preservative have aimed at producing water-insoluble compounds in the wood from mixtures that are water-soluble at the time of treatment.

Zinc Chloride.—The best results are obtained by an impregnation treatment, such as a pressure process. A common strength for the solution is 3 to 5 per cent.; at high concentrations the wood substance is attacked, and it is therefore not advisable to use solutions stronger than 5 per cent. Zinc chloride solutions are slightly more corrosive than creosote solutions to iron and steel.

Sodium Fluoride.—This is the basis of several proprietary preservatives of Continental origin. Solutions of 2 to 4 per cent. in soft water are commonly used; a 4 per cent. solution is practically saturated at ordinary temperatures.

Magnesium Silicofluoride.—The salts of hydrofluosilicic acid are toxic to wood-destroying fungi; the magnesium salt is the one generally used, owing to the relative insolubility of the others. It should not be used in contact with metal or glass.

Copper Sulphate.—Although toxic to wood-destroying fungi, copper sulphate has the disadvantage of low permanency on account of its high solubility. It is not much used in this country, probably because its action upon iron prevents it being used in ordinary treating plants.

Mercuric Chloride.—This salt formed the basis of the Kyanising process. Its extreme toxicity to human beings and animals and its corrosive action account for its not having been used to any extent in this country.

Arsenic.—Arsenic in various forms has been a common ingredient of preservatives for protecting timber against the attack of white ants. It is unlikely to be used much in this country because of its poisonous character.

Recent Developments in Water-soluble Preservatives.—The use of zinc meta-arsenite (Z.M.A.) has been suggested by Curtin. Although insoluble in water, it is soluble in dilute acids, so that by using an acetic acid solution of the salt, the preservative is slowly deposited in the wood as the acid evaporates.

It has been found that alkali dichromates are able to fix certain salts in wood, and wood preservative salt mixtures containing alkali chromates have therefore been patented.

C. Solvent Type Preservatives.—On the whole these preservatives, especially those containing solvent naphtha, penetrate the wood somewhat better than the other types, and are thus more suitable for methods of spraying or brushing the timber. A drawback is that they are relatively more expensive than the other types.

Toxic chemicals used include metallic salts or metallic (especially copper and zinc) salts of organic acids such as naphthenic, abietic and oleic acids, phenols such as β-naphthol, chlorinated phenols and hydrocarbons such as chlorinated naphthalene.

Patented and Proprietary Preservatives.—Frequently extravagant claims are made for these preservatives without due regard to the comparatively small protection afforded the timber by the slight penetration resulting from a surface application. All the types previously mentioned are represented in this class of preservatives, but so far as this country is concerned the oil type predominates. Many of that type are derived from coal- or wood-tar or mixtures of these, and are generally refined to produce oils that are cleaner and more penetrating than ordinary creosote. Frequently, certain substances are taken out of the distillates to ensure that they are fluid at ordinary temperatures and to increase their penetrating properties. Sometimes pigments or dyes are added to give a decorative value. Speaking generally, the preservatives manufactured by reputable firms are efficient and can be safely used.

Conference on Atmospheric Pollution

On June 1st thirty-eight representatives of local authorities and other organisations co-operating with the Department of Scientific and Industrial Research met at the offices of the Department in the half-yearly conference. The gathering included representatives from Barnsley, Birmingham, Dagenham, Glasgow, Halifax, Hull, Leicester, Liverpool, London, Manchester, Newcastle, Rotherham, Salford, Scarborough, Sheffield, Stoke-on-Trent, Walsall, Westminster, Willesden, Wolverhampton, The British Electrical Development Association, The British Commercial Gas Association, Messrs. Cadbury Bros. and The Thames Nautical Training College.

In the absence, owing to indisposition, of the Chairman (Mr. W. Brownhill Smith, M.V.O., D.L.), Dr. H. A. Des Voeux, a past Chairman, presided.

Dr. G. M. B. Dobson, F.R.S., Chairman of the Atmospheric Pollution Research Committee, presented the usual report on the progress of the investigations carried out under the Committee. The Conference noted in particular that systematic observations in connection with the intensive survey of the pollution in and around the City of Leicester were begun on April 1st. During the preceding four months the Survey staff were occupied in installing different standard measuring apparatus at twelve sites and in certain trial routine observations. The Conference were very appreciative of the generous help afforded by the authorities at Leicester in starting the work. The decision of the authorities to equip and maintain a station for regular meteorological observations was greatly welcomed.

The Conference also recorded their appreciation of the valuable assistance given by the Public Analysts of Glasgow, Hull and Sheffield, in an investigation of the possibility of combining a dust filter with apparatus for the volumetric determination of sulphur dioxide in the atmosphere. This was regarded as an excellent illustration of the value of the collaboration of co-operating bodies with the Research Committee in work of this kind.

The Conference were glad to receive a report submitted through the Medical Officer of Health for Leeds on the analysis of dust samples collected in Leeds, Halifax and Huddersfield.

The Conference endorsed a proposal of the Research Committee that a meeting of Public Analysts and others who are directly responsible for making observations on behalf of co-operating bodies should be convened to discuss technical problems and to interchange ideas on the measurement of atmospheric pollution.

Mr. Brownhill Smith retired from the Chairmanship of the Conference, having served for three consecutive years, the maximum period permitted by the Rules and Standing Orders. Alderman David Adams, M.P., J.P., a representative of Newcastle-upon-Tyne, was elected Chairman for the ensuing year.

Trinidad and Tobago

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1936

In his Annual Report, Mr. H. S. Shrewsbury states that 4376 samples were examined for various Government Departments, and 117 for private firms and persons. As there are no consulting analysts in local practice, private samples may be examined on payment of a fee, but such work is of secondary consideration to Government work. Of the 1055 samples examined under the Food and Drugs Ordinance, 277 were of milk, 316 of aerated waters, 143 of coffee and 124 of butter.

Adulteration of Coffee.—It was not until 1932 that coffee was found to be adulterated in Trinidad (*cf.* Analyst, 1933, **58**, 696). In 1936 eight of the 143 samples examined were adulterated. In 1935 the adulterant was burnt sugar, whilst in 1936 burnt sugar and starchy materials were used.

Friolene Oils.—Eighty-two samples of Friolene and Buttercup oils (derived from coconut oil) were examined; two were adulterated with olive oil, which is more expensive.

Food Poisoning: Its Epidemiology and Bacteriology*

At the Ministry of Health 58 outbreaks of food poisoning were recorded in 1934 and 129 in 1935. They are discussed under three headings: (1) those due to the multiplication, within the body, of pathogenic bacteria present in food—the "infection" type; (2) those due to the ingestion of certain substances formed as the result of bacterial multiplication in the food before ingestion—the toxin type; (3) those due to the toxin of *Clostridium botulinum*—botulism.

(1) *The "Infection" Type.*—Among the organisms responsible for this type, members of the *Salmonella* group are the most common (*cf.* Savage and Bruce White, Analyst, 1925, **50**, 341), but members of the Dysentery group (Sonne and Flexner) must be included. In 1935 the former were responsible for 53 and the latter for 12 outbreaks, 8 being attributable to the Sonne bacillus, and in 1936 an outbreak due to *B. proteus* (*cf.* Analyst, 1925, **50**, 556) was recorded by Gray. From antigenic analysis it is justifiable to place typhoid and paratyphoid bacilli in the *Salmonella* group, but generally, and almost invariably, the symptomatology and epidemiology of typhoid and paratyphoid infections are very different from those of the food-poisoning bacilli. A few instances, however, have been recorded of bacilli of the *Salmonella* group giving rise to symptoms similar to those caused by typhoid and paratyphoid bacilli, *i.e.* continued fever, as opposed to acute gastro-enteritis, and *vice-versa*. The bacillus most commonly responsible for food poisoning outbreaks is *Bact. typhi-murium* (*B. aertrycke*); during the decade 1923–1933 the Ministry of Health found this organism in 110 of 186 outbreaks.

(2) *The "Toxin" Type.*—Notwithstanding exhaustive investigations into many outbreaks, it has not been possible to isolate any toxins produced by members of the food-poisoning or dysentery groups. These outbreaks were formerly

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* Paper by E. R. Jones, M.D., D.P.H., F.I.C. (Senior Pathologist, Kent County Council), read at the Congress of the Royal Institute of Public Health and Institute of Hygiene, Margate, 1937; *Brit. Med. J.*, July, 1937, p. 106.

designated as ptomaine poisoning, but the ptomaines or toxic amines are not produced until food reaches an advanced stage of decomposition, and they are relatively non-toxic, except in very large doses. Potent toxins, however, are produced by certain strains of *Staphylococcus albus* and *aureus* under certain conditions; it has been suggested by Savage, with considerable experimental support (*cf.* ANALYST, 1927, **52**, 123), that similar toxins are elaborated by members of the *Salmonella* group, that the bacilli are killed in the cooking, but that the toxins survive and cause food poisoning. Bacteria capable of giving rise to toxic substances under certain conditions are not confined to these two groups, among them may be mentioned *B. coli*, *Proteus vulgaris*, *Proteus Morgani*, *Streptococcus viridans*, and a micrococcus found in milk. The common ways in which food may be infected are as follows:

(*a*) Infected animals may be used for food; for example, meat (beef and pork), ducks or their eggs (*cf.* Scott, ANALYST, 1930, **55**, 595). (*b*) Infected animals (*e.g.* rats, mice and bovines) may excrete specific organisms that contaminate food. (*c*) Human carriers may contaminate the food by handling.

(3) *Botulism.*—The causative organism, *Cl. botulinum*, is a normal inhabitant of the surface layers of soil. It is incapable of growth in the animal body and of giving rise to infection, but under certain conditions it produces a very potent toxin. The spores are very resistant to heat; the potted duck paste in the Loch Maree cases had been heated on three occasions, and at one stage to 115° C. for 2 hours (*cf.* ANALYST, 1923, **48**, 118). The toxin is destroyed by such heat as is ordinarily applied in cooking. In Europe most cases have been caused by preserved meat or meat paste; in America by canned vegetables and occasionally by canned fruits.

D. R. W.

British Standards Institution

BRITISH STANDARD SPECIFICATION FOR PORTABLE CHEMICAL FIRE EXTINGUISHERS: FOAM, AND CARBON TETRACHLORIDE, TYPE

THIS Specification (No. 740—1937) is supplementary to B.S. No. 138 (Portable Chemical Fire Extinguishers, Acid Alkali Type). It has been approved by the Chemical Engineering Industry Committee and endorsed by the Engineering Divisional Council, and is intended to include the technical provisions necessary for the supply of the articles referred to.

(1) The Foam type is one in which the pressure required to eject the liquid contents is generated by the chemical action of a solution of an acid salt stored in an inner receptacle, in conjunction with a carbonate or bicarbonate solution in combination with a stabiliser, stored in the outer container of the extinguisher. A foam is produced by the combination of the "inner" and "outer" solutions.

(2) In the carbon tetrachloride type, carbon tetrachloride is propelled from the extinguisher by means of (*a*) hand force pump mechanism; (*b*) release of compressed carbon dioxide or nitrogen from an attached cylinder; (*c*) pressure of carbon dioxide stored in the carbon tetrachloride container; (*d*) pressure of air from a self-contained air pump.

Reference is directed to B.S. No. 575—Carbon Tetrachloride.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Diacetyl in Butter. J. Pien, J. Baisse and R. Martin. (*Le Lait*, 1937, 17, 673–698.)—A new method for the determination of diacetyl in butter is described. The apparatus consists of a 300-ml. flask fitted for steam-distillation and connected with a Liebig condenser by means of a long upright tube having a constriction followed by a bulb near the upper end. The condenser outlet is attached to an adapter which is drawn out to a capillary reaching almost to the bottom of an Esbach tube. The butter (50 to 100 g.) is placed in the flask and 0·5 ml. of water in the Esbach tube. The sample is distilled with steam until 10 ml. of distillate have been collected in the Esbach tube, which is then removed and replaced by a similar tube, and a second 10 ml. is collected. The distillate in each tube is treated with 0·5 ml. of a freshly prepared solution of diaminobenzidine (2·5 per cent.), and the liquids are well mixed. To the mixture 0·5 ml. of conc. hydrochloric acid is added, and the whole is again well mixed. After 2 minutes the colour is compared with that of a standard solution of potassium dichromate which is a dilution of a 1 per cent. solution, but the dilutions are not in linear relationship to the diacetyl with which they correspond, and a table in the original paper should be consulted. The amount of diacetyl present in butter showed no significant variation with the season of the year, nor with the district from which it was obtained, but, as was already known, was dependent on the methods of separating the cream and preparing the butter. During the distillation the flask is not heated directly, and the steam current is so regulated that the rising vapours from the flask have to bubble through condensate in the bulb. Under these conditions all the diacetyl can be obtained in the first 10 ml. of distillate, and the second 10 ml. should contain none. (See also Barnicoat, ANALYST, 1935, 60, 653.) S. G. S.

Physico-Chemical Investigation Incidental to the Study of Chocolate Fat Bloom. Part I. W. Clayton, S. Back, R. I. Johnson and J. F. Morse. (*J. Soc. Chem. Ind.*, 1937, 56, 196–199T.)—Oxidised cocoa butter has the property of inhibiting fat bloom in chocolate and the deposition of stearine in chilled olive oil. Air is blown through cocoa butter at 250° C. until the iodine value is about 20, the molecular weight meanwhile increasing from 890 to about 1600. Blown cocoa butter is regarded as of polar character—mainly a polymerisation product of oxidised oleo-disaturated glyceride, the structural unit being probably a dimeride. Confirmation of the polar type of molecular structure was obtained by means of the surface film technique of Langmuir and Adam. The presence of blown cocoa butter slightly depresses the complete fusion point of ordinary cocoa butter and has a marked effect on the solidification, which takes place without the usual formation of clumps of crystals. The blown fat is regarded as exhibiting a definite balance between hydrophylic and hydrophobic molecular groupings which lead to adsorption-orientation phenomena. To determine the influence of blown cocoa butter and of lecithin on fluidity (1) 0·6 per cent. of the blown fat and (2) 0·6 per cent. of lecithin were added, respectively, to systems of (*a*) cocoa, 135 g., and fat, 40 g.; (*b*) sugar, 160 g., and fat (cocoa butter), 55 g.; (*c*) dry milk powder, 300 g., and fat (cocoa butter), 185 g.; (*d*) moist milk powder and fat (30 ml. of water were added to (*c*)), and the increase of mobility was measured. Percentage increases were:—*a*, (1) 127, (2) 33; *b*, (1) 26, (2) 89; *c*, (1) 280, (2) 520; *d*, (1) 220, (2) 270. Blown cocoa butter is thus superior in the hydrophobic, and lecithin in the hydrophylic systems.

The addition of quantities up to 1 per cent. of blown cocoa butter to normal olive oil, which is then chilled to 2 to 4° C., inhibits the deposition of stearine according to the amount of blown fat and its iodine value. Whilst the control oil set solid in a few hours, the treated oil remained clear and fluid for 4 years (the duration of the experiment). It was found that the capacity of blown cocoa butter to inhibit stearine deposition runs quantitatively parallel with its efficacy in preventing fat bloom in chocolate, and it is suggested that the same physico-chemical cause operates to prevent crystallisation in chilled olive oil and stored chocolate. The formation of bloom in nut-centred chocolates is not completely inhibited by even the best blown cocoa butter (although it is greatly reduced), possibly because there may be interference due to preferential adsorption at the fat crystal—fat interface by the nut oils. D. G. H.

Siene Bean and Oil. T. S. Perrin. (*J. Amer. Chem. Soc.*, 1937, **59**, 1401–1402.)—The Siene bean plant (*Daubentonio longifolia*), sometimes called the "coffee bean" or "rattle box," grows abundantly inland and along the Gulf Coast of Texas and Florida and may attain the size of an average peach tree. The trees are hardy and bear prolifically, the pod containing 4 to 8 seeds, which are extremely toxic to sheep and (in the laboratory) to guinea-pigs. The water-soluble portion of the seeds (17·5 per cent.) formed a foaming soap-like emulsion, and contained 2·3 per cent. of protein calculated on the original sample. The soluble substances gave negative results in tests for sugar and starch, but on hydrolysis the original sample was found to contain 8·6 per cent. of sugar (calculated as dextrose). The seeds contained:—Moisture, 11·7; fat, 3·8; starch, 27·9; protein, 21·2; fibre, 17·7; ash, 2·8; non-protein water-soluble matter, 15·2 per cent. The crude oil, as extracted with ether, had: sp.gr. at 25/25° C., 0·9209; n_{D}^{25}, 1·4730; saponification value, 194·2; iodine value (Hanus), 97·3; acetyl value, 6·9; acid value, 4·5; unsaponifiable matter, 3·0 per cent.; it contained 13·8 per cent. of saturated acids and 78·4 per cent. of unsaturated acids (iodine value, 120·6). D. G. H.

New Purine in Tea. T. B. Johnson (*J. Amer. Chem. Soc.*, 1937, **59**, 1261–1264.)—Concentrated tea residues from the commercial removal of caffeine were treated with warm methanol, and the extract, when filtered and cooled, deposited hexagonal crystals, which were picked out mechanically and purified by crystallisation from boiling water. The substance, which was characterised by its crystalline structure, sharp m.p. (225° C.) and neutral reaction, was identified as 1, 3, 7, 9-tetramethyl-2, 6, 8-trioxypurine. It is, in fact, the first methylated derivative of 2, 6, 8-trioxypurine (uric acid) to be discovered in nature. This purine (tetramethyl uric acid) was first synthesised by Emil Fischer (*Ber.*, 1884, **17**, 330, 1784), and was afterwards described by Reuter (*Ber.*, 1897, **30**, 3009). The crystallographic characteristics of the present material, isolated from tea, agree exactly with those in Reuter's description. D. G. H.

Biochemical

Simple Method for the Determination of Acetone in Blood and Urine. J. C. Abels. (*J. Biol. Chem.*, 1937, **119**, 663–667.)—The apparatus consists of a 50-ml. Erlenmeyer flask having a tightly fitting cork. Suspended from the under surface of the cork by means of a pin is a 1-cm. length of cotton pencil, which is a compressed roll of cotton used by dentists. The urine is made acid to Congo red with a 1:1 solution of sulphuric acid, and 0·5 ml. is pipetted on to the cotton roll. With blood no previous acidification is necessary, and 0·5 ml. of the sample may be used directly. Over the bottom of the flask 0·5 ml. of a 5 per cent. solution of sodium bisulphite is spread, and the cork is carefully and firmly inserted, so that the blood or urine sample is suspended about 1 cm. above the level of the bisulphite. The flask is heated in a boiling water-bath for 15 minutes and, after cooling, the cork and cotton roll are removed. One ml. of water is added, then 1 ml. of Nessler's reagent, bringing the total volume to 2·5 ml. The liquid is poured into a test-tube (6 in. × 0·5 in.), and the turbidity is compared with standards. These standards are prepared at the same time in similar test-tubes from 0·002, 0·004 . . . . 0·010 mg. of acetone, water to 1 ml., 0·5 ml. of 5 per cent. sodium bisulphite solution and 1 ml. of Nessler's reagent. The full development of the turbidity requires 15 minutes. Standards will keep for 24 hours if exposed to light as little as possible. The amounts of acetone in blood ranged from 0·3 to 2·0 mg. per 100 ml., and in urine from 0·2 to 2·5 mg. per 100 ml. Recovery of added acetone was from 90 to 110 per cent. S. G. S.

Titrimetric Method for the Quantitative Determination of Lead in Biological Materials. M. K. Horwitt and G. R. Cowgill. (*J. Biol. Chem.*, 1937, **119**, 553–564.)—The lead is extracted from aqueous solution by means of dithizone in chloroform and the extract is freed from excess of dithizone by shaking with aqueous cyanide solution. The lead dithizone complex in the chloroform is then decomposed by shaking with aqueous acid, which removes the lead and leaves in the chloroform the equivalent amount of dithizone. This is titrated with standard lead solution as follows:—The solution of dithizone in chloroform is mixed with dilute cyanide solution, which removes most of the dithizone from the chloroform, imparting a brown colour to the aqueous layer. A lead solution is added from a burette to this mixture until all the dithizone has been re-converted into lead dithizonate, as indicated by the disappearance of the brown colour in the aqueous layer and the absence of a red colour when the aqueous layer is mixed with chloroform and additional lead solution. The dithizone reagent is prepared by dissolving 40 mg. of diphenylthiocarbazone in 400 ml. of chloroform and filtering the solution into a 500-ml. separating funnel. To this are added 50 ml.

of water containing 2 ml. of 25 per cent. hydroxylamine solution, and the whole is shaken. The funnel is kept in a cool dark place, and the chloroform solution is withdrawn as required. The potassium cyanide solution is 0·5 per cent. and is prepared from a 10 per cent. solution which is itself prepared fresh each day. It is essential that the dilute cyanide solution shall be lead-free, and this is ensured by extracting it with chloroform containing dithizone. A stock solution of lead nitrate containing 10 mg. of lead per ml. is also required (1·599 g. of lead nitrate per 100 ml.), and from this a dilute solution containing 0·01 mg. of lead per ml. is prepared. A 20 per cent. solution of sodium citrate is also required, and 800 ml. of this are treated with 8 ml. of 10 per cent. potassium cyanide and extracted with 15-ml. portions of the dithizone solution until free from lead. The citrate mixture is then washed with 25-ml. portions of chloroform and acidified with 4 ml. of 20 per cent. hydrochloric acid, and the extraction of the excess of dithizone is completed with 20-ml. portions of chloroform.

For the determination of lead in blood, 10 ml. of the sample are dried in a 50-ml. silica dish, and the residue is charred. It is then heated in a muffle furnace at about 475° C. for 2 hours, after which the dish is removed. The ash is moistened with 2 ml. of re-distilled nitric acid and warmed until the excess of acid has been driven off, and the dish is returned to the muffle for about half-an-hour. The dish is then placed on a hot-plate, 15 ml. of 20 per cent. hydrochloric acid solution are added carefully, and the whole is heated until the ash is dissolved. The solution is washed into a 125-ml. separating funnel with about 20 ml. of hot water. Ten ml. of 20 per cent. sodium citrate solution and 3 ml. of strong (re-distilled) ammonium hydroxide solution are added to the silica dish, and the contents are well mixed and transferred to the separating funnel with sufficient water to give a total volume of about 75 ml. The contents of the funnel are cooled, 1 ml. of a 25 per cent. solution of hydroxylamine hydrochloride and 1 drop of phenol red solution are added and the whole brought to *p*H 8·0 by the addition of ammonium hydroxide from a burette. The solution is again cooled and to it is added, drop by drop with shaking, 0·5 ml. of 10 per cent. potassium cyanide solution. The mixture is immediately extracted with 0·5 ml. of the dithizone solution and 4 ml. of chloroform. If, after shaking, the chloroform layer does not contain a noticeable excess of dithizone (green colour), further 0·2 ml.-portions are added, and the funnel is shaken, until an excess is present. The chloroform phase is removed to another separating funnel and the aqueous phase is extracted twice more with 0·2-ml. portions of dithizone solution and 2-ml. portions of chloroform. To the combined chloroform solutions 0·5 per cent. potassium cyanide solution is added in such quantity that the volume of the cyanide solution is 1·5 times the volume of the chloroform, and the whole is shaken for 10 seconds. The chloroform layer is transferred to another separating funnel, and the cyanide solution is extracted with 1 ml. of chloroform to recover any traces of lead complex in it. The combined chloroform extracts are again extracted with 1·5 times their volume of 0·5 per cent. cyanide solution, and any lead taken up in this is recovered by extraction with 2 ml. of chloroform. The lead is removed from the red dithizone complex by shaking the combined chloroform extracts for 15 seconds with 2 volumes of 0·5 per cent. hydrochloric acid. The green chloroform layer is withdrawn, and the acid aqueous solution is again shaken with 1 ml. of chloroform. The chloroform extracts are combined. This chloroform solution of dithizone is then treated with 0·5 volume of 0·5 per cent. cyanide solution and shaken. Most of the dithizone goes into the aqueous layer, giving it a brown colour. Dilute standard lead solution is added from a burette, drop by drop, with shaking after each addition, until only a faint colour remains in the aqueous phase. The red chloroform phase is discarded, and the aqueous layer is washed with chloroform, 2 ml. at a time, until, after shaking, the chloroform layer remains colourless. A drop or two of the lead solution is added, and the whole is shaken for 5 seconds. The pink chloroform solution is withdrawn, and the aqueous layer again extracted with 2 ml. of chloroform, plus a drop or two of the lead solution, until the further addition of lead no longer imparts a pink colour to the chloroform after shaking.

To determine lead in urine, 200 ml. are ashed in a 250-ml. silica dish, as described above, but 5 ml. of nitric acid are used. The ash is moistened with 15 ml. of 20 per cent. hydrochloric acid and heated until almost dry. It is then transferred to a 500-ml. separating funnel with the aid of 15 ml. of the hydrochloric acid, 50 ml. of the sodium citrate solution and 5 ml. of ammonium hydroxide solution. The volume is made up to 250 ml. and, after being cooled and treated with one drop of phenol red solution, the reaction is adjusted to *p*H 8·0, as described. Three ml. of 10 per cent. potassium cyanide solution are now added, and the liquid is extracted with an excess of dithizone, 0·5-ml. portions and 3 ml. of chloroform being used. The procedure is then as described above.

The lead-content of bone is determined by heating the dried bone for 2 hours in a silica dish in the muffle at 475° C. The dish is removed, an amount of nitric acid equivalent to 3 ml. for each 1·5 g. of bone is added, and the mixture is carefully evaporated to dryness. The dish is heated in the muffle for a further half-hour. The contents of the dish are then dissolved in 20 per cent. hydrochloric acid, 15 ml. for each 1·5 g. of dried bone taken, and an aliquot part equivalent to not more than 1·5 g. of dried bone is transferred to a 500-ml. separating funnel. To this are added 75 ml. of the sodium citrate solution, 2 drops of phenol red solution, and sufficient water to give a volume of 350 ml., and ammonium hydroxide is then carefully added, with shaking and cooling, to give a *p*H of 8·0. Five ml. of 10 per cent. cyanide solution are added slowly, and the mixture is extracted with *excess* of dithizone. Three ml. of dithizone solution and 3 ml. of chloroform are added, and the whole is shaken for 30 seconds. If the chloroform layer is not purple, more dithizone—1 ml. at a time—is added until a purple colour persists. The chloroform layer is transferred to a 125-ml. separating funnel, and the aqueous layer is extracted three times, first with 1 ml. of dithizone solution plus 2 ml. of chloroform, then with 0·5 ml. of dithizone plus 2 ml. of chloroform, and finally with 3 ml. of chloroform. The chloroform extracts are combined and extracted once with twice their volume and twice with an equal volume of 0·5 per cent. potassium cyanide solution. The lead is removed from the dithizone complex by washing with 2 parts by volume of 0·5 per cent. hydrochloric acid, and the titration is carried out as described for blood.

All the glassware (including burettes) should be of Pyrex and a blank determination should be made for each type of material. Recovery of lead added to the various materials in quantities of 0·001 to 0·15 mg. ranged from 90 to 100 per cent. Beef blood (without addition of lead) contained 0·00016 mg. per ml., human urine 0·00003 mg. per ml., and bone ash 0·0085 mg. per g. S. G. S.

Metabolism of Organic Acids of Tobacco Leaf during Culture. G. W. Pucher, A. J. Wakeman and H. B. Vickery. (*J. Biol. Chem.*, 1937, **119**, 523–534.)—The three chief organic acids of tobacco leaf—malic, citric and oxalic acids—undergo very little change in absolute amount during culture of the leaves in the light, although extensive photosynthesis occurs. The total organic acidity also remains essentially constant. During culture in the dark the amount of malic acid diminishes and that of citric acid increases, other acids remaining unchanged. It is suggested that the additional citric acid is formed directly from the malic acid. S. G. S.

Metabolism of the Proteins of Different Parts of the Wheat Grain compared with that of Casein. H. Jordan. (*Z. Unters. Lebensm.*, 1936, **72**, 457–460.)—Kaping (*Z. Unters. Lebensm.*, 1936, **72**, 453), by determining the ratio of carbon to nitrogen and of "vacat-oxygen"* to nitrogen in urine, compared the metabolic functions of the proteins of wheat gluten with those of casein. The investigation has been extended to the proteins in the separate parts of the wheat grain, *viz.* the germ, the flour and the bran. According to Kaping (*loc. cit.*) gluten protein approximates most nearly in feeding value to casein. If, however, the feeding is continued for a long period, with gluten as the source of nitrogen in the diet, the nutritional value in comparison with casein diminishes and the body-weight, which remains constant for a time, ultimately shows a slight diminution. The nitrogen balance also shows that slightly less nitrogen is being retained than with a casein diet. In the author's experiments, which were confined to periods of one week, the nitrogen absorption with casein diets and gluten diets showed little difference, the C : N and "vacat-O" : N ratios in urine being almost identical. The procedure consisted in feeding rats with diets the ingredients of which were identical, except that different proteins were used as the source of nitrogen. The constant ingredients of the diets were cod-liver oil, sugar, potato starch, mineral salts, orange juice and water. The variable sources of nitrogen were casein, wheat germ, wheat gluten (in the form of a commercial preparation "Glidin"), wheat bran and egg albumin. Each diet contained approximately the same amount of protein (9·4 per cent. on the dry substance) and had an energy value of 47 calories per animal. The urine and faeces were collected and analysed, the following determinations being made and expressed as an average value per animal per day:—urine carbon, urine "vacat-oxygen," urine nitrogen and faeces nitrogen. From these were calculated the ratio of carbon to nitrogen and of "vacat-oxygen" to nitrogen, and the nitrogen balance was determined. Nitrogen was determined by a semi-micro Kjeldahl method, carbon by the microchemical method of Nicloux-Osuka (Osuka, *Biochem. Z.*, 1932, **244**, 284), and the "vacat-oxygen" by the microchemical method of Müller-Kanitz (*Biochem. Z.*, 1932, **249**, 234). The results of the experiments were as follows:—The nitrogen balance was almost equal in all experiments, except that with wheat bran as the source of nitrogen it was higher than with other proteins. The nitrogen in the faeces was highest on the diet containing wheat germ, then followed the bran diet, the remaining diets yielding almost equal amounts of faecal nitrogen. With wheat germ diet the urinary quotients were distinctly higher, and highest of all with the bran diet. Similar experiments by Bickel, Sander and Schilling (*Münch. Med. Woch.*, **1935, 37, 1482**) show that these high values are also given by rye bran. The amount of dry faeces was highest on the bran diet. This is due to the high cellulose-content of bran. The amount of faeces on the wheat germ diet, although less than on the bran diet, was higher than on the other diets; apparently the commercial germ preparation used contained much cellulose. The experiments show that when the proteins of the different parts of the wheat grain are used as the sole source of nitrogen in a balanced diet, the urinary quotients show different values.

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* "Vacat-oxygen" is a measure of the oxidisable substances in urine which can be determined by reduction of iodic acid (Kaping, *Z. Unters. Lebensm.*, 1936, **72**, 455).

A. O. J.

Nutritive Value of Bread. A. L. Baker, M. D. Wright and J. C. Drummond. (*J. Soc. Chem. Ind.*, **1937, 56, 191T–194T.**)—The nutritive value of bread was studied with regard to its content of vitamin B, and particularly of the component B_1. Wheat itself from various sources contained between 2·0 and 2·5 units of vitamin B_1 per g. In stone-ground wholemeal flour 64 per cent. of the original vitamin B_1 in the wheat was found in the flour, about 13 per cent. in the bran, and 23 per cent. in the middlings. Flour from a modern mill contained 5 per cent. of the original vitamin B_1 in the flour, 70 per cent. in the sharps, 19 per cent. in the bran, and 6 per cent. in the germ. Samples of bread showed a wide range of values—from London white bread at 0·14 unit per g. to wholemeal bread at 1·2 units per g. Germ-bread contained 1·7 units per g. From enquiries made by the authors they have calculated that wholemeal bread constitutes about 18 per cent. of the total bread consumption of well-to-do families, but only about 5 per cent. of that of poor families, and since bread is the staple food of the poorer classes, a vitamin B_1 deficiency is to be anticipated amongst these people. The authors are engaged in a survey of the medical literature in order to ascertain if the commonly occurring disorders, such as constipation and gastric troubles, can be correlated with the decrease of vitamin B_1 ingested in bread, as compared with that a century ago. (See also succeeding abstract.) S. G. S.

Vitamin B_1 Content of Bread and Flour. L. J. Harris and P. C. Leong. (*J. Soc. Chem. Ind.*, 1937, **56**, 195T–196T.) (See also preceding abstract.)—Various kinds of bread and flour were examined for vitamin B_1 content. The results indicated that commercial white bread contained 0·15 unit per g., "germ" bread 0·8 unit per g., and proprietary wholemeal bread 0·75 unit per g. Wholemeal bread from an experimental bakery contained 0·9 unit per g., "with germ" brown bread from the same source 0·8 to 0·9 unit per g., "without germ" brown bread 0·65 to 0·8 unit per g., and "bran" bread 0·5 unit per g. Flours ranged from 0·2 unit per g. for white flour to 1·5 units per g. for wholemeal; wheat germ contained from 6·0 to 9·6 units per g. The authors conclude that "bran" bread or brown bread without the germ is not much inferior to genuine wholemeal bread, and is greatly superior to white bread in its vitamin B_1 content. "Germ" bread and "germ" flour are less potent than might have been imagined and are but little superior to ordinary wholemeal. Soil treatment appears to have little significant effect on the vitamin B_1 content of wheat or barley (Harris, *J. Agric. Sci.*, 1934, 24, 410). S. G. S.

Reactions of Ascorbic Acid. G. Woker and I. Antener. (*Helv. Chim. Acta*, 1937, 20, 732–741.)—The similarity between ascorbic acid and Schardinger's enzyme has been reported previously (*Helv. Chim. Acta*, 1937, 20, 144; Abst., ANALYST, 1937, 321). The present paper describes the reactions between ascorbic acid and various reagents. Ascorbic acid reduced a solution of picric acid and picrate to picramic acid in the cold. Other reducing substances commonly present with ascorbic acid (glutathione, cystein and creatinine) reduce the mixture only on warming. The reduction of iodate to hydriodic acid by ascorbic acid is already known. The hydriodic acid will react with excess of iodate to liberate free iodine, which can be made to oxidise benzidine to benzidine blue. This can be made the basis of a quantitative test, and the limit for the reaction is 0·0000172 g. of ascorbic acid. It is possible that this reaction may be utilised for the estimation of thyroxine. Ascorbic acid will reduce quinone to quinhydrone and, in addition, will give the furfural reaction with a suitable redox system. Dehydroascorbic acid will react in a similar manner to give β- or β′-hydroxyfurfural. A green colour is obtained with orcinol in pure nitric acid and a yellowish-orange colour with phloroglucinol in the same acid. The limits of the reactions are 0·000176 g. and 0·000035 g. of ascorbic acid respectively. A positive reaction is also obtained with α-naphthol (Molisch's reaction), with a limiting value of 0·0000176 g. of ascorbic acid. Dehydroascorbic acid reacts with phenylhydrazine to give an osazone.

S. G. S.

The Titration Method for Vitamin C. L. J. Harris. (*5th Internat. Tech. & Chem. Congress Agricult. Industries.*)—The points to be watched in the determination of vitamin C by titration with 2, 6-dichlorophenolindophenol are (*a*) that proteins should be removed and a clear solution obtained by means of grinding with sand and trichloroacetic acid, although this may be omitted with certain clear fruit juices; (*b*) that extraction should be carried through and the titration of the extract begun with as little delay as possible; (*c*) the solution should be titrated at an acid reaction, and (*d*) the titration end-point should be reached within two minutes. Previously reported interfering substances and various modifications of the method are described, but it is concluded that simple titration gives surprisingly accurate results without the necessity for further modifications and complications; and although theoretically the method is not absolutely specific, few exceptions are actually encountered in every-day experience. S. G. S.

"Ascorbic Acid Oxidase" in Relation to Copper. E. Stotz, C. J. Harrer and C. G. King. (*J. Biol. Chem.*, 1937, 119, 511–522.)—The catalytic activity of squash and cauliflower juices on the oxidation of ascorbic acid, previously ascribed to a specific oxidase, is now stated to be due to the copper present in combination with protein material. Diethyldithiocarbamate, 8-hydroxyquinoline, pyridine and potassium thiocyanate, sodium cyanide, potassium ethylxanthate, potassium ferrocyanide and sodium sulphide acted as copper inhibitors and produced nearly complete poisoning of the "enzymes" as well as of inorganic copper and copper-protein mixtures. These inhibitors did not affect the catalytic function of nicotine-haemochromogen in a manner that would suggest that this type of substance is responsible for the oxidation of ascorbic acid by cauliflower juice or "purified squash oxidase." The catalytic properties of copper are considerably altered by the presence of proteins. A mixture of copper and albumin exhibits the characteristic properties of the "enzymes," with an optimum *p*H similar to that of the "enzymes," being inactivated by heat and acids, and showing similar velocity reactions to the quantity of substrate. The type of union between copper and protein is similar to that in copper amide, biuret, and copper haematophorphyrin. Although the work described in this paper was done only with cauliflower juice, "purified squash oxidase," cucumber juice and cabbage juice, it is suggested that other "ascorbic acid oxidases" which have been described are not essentially different from these. S. G. S.

Bacteriological

Detection of *Microbacterium tuberculosis* in the Air and Dust by a Simple Technique. G. M. Eisenburg. (*Amer. J. Hyg.*, 1937, **24**, 138–146.)—The author proves experimentally that living virulent tubercle bacilli are present in the air and dust of tuberculous environments. The investigation comprised the examination of rooms in four hospitals. Sterile evaporating dishes, 10 cm. in diameter, containing 20 ml. of sterile saline, were placed in the four corners of each room for 7 days. The contents of each dish, with washings, were then centrifuged in a separate tube and concentrated to 1 ml. Smears were made from this concentrate and examined microscopically; the remainder was subjected to digestion with an equal volume of 2, 3 and 5 per cent. oxalic acid solution for 30 minutes at 37° C., and centrifuged for 10 minutes at 3000 r.p.m., and the sediment was washed with sterile saline and again centrifuged and concentrated to 1 ml. Cultures were then made from the resulting concentrates. The remainder of the concentrates from each institution were pooled, and several guinea-pigs were inoculated from each of the four groups. Four culture media were used, *viz.* those of Petroff, Petragagni, Corper and Uyei, and Sweany and Evanoff. The first three were found to be good and are given in order of merit. The last was found to be unsatisfactory inasmuch as it allowed contaminating micro-organisms to grow.

The results, which were remarkable, may be summarised as follows:—Number of rooms tested, 15; number of samples, 55; percentage of smears showing acid-alcohol-fast bacilli, 88; number of primary cultures, 230; per cent. lost by contamination, 39; number of primary cultures remaining, 140; percentage number of primary cultures showing tubercle bacilli, 47. It will thus be seen that a large number of positive results were obtained by microscopical examination, and it is suggested that possibly much has been overlooked by earlier investigators. The number of positive results obtained by culture, *viz.* 47 per cent., shows that a considerable number of the acid-alcohol-fast bacilli were living tubercle bacilli. All the guinea-pigs inoculated were infected with tubercle bacilli. Inoculations were also made from the pooled cultures (after sub-cultivation) from each institution. It is suggested that the air and dust of tuberculous environments may constitute a potential menace to the health and well-being of healthy individuals in constant contact with them. D. R. W.

Measurement of the Size of Viruses by High-speed Centrifuging. J. McIntosh and F. R. Selbie. (*Brit. J. Exper. Path.*, 1937, **18**, 162–74.)—A description is given of the super-centrifuge employed. It is constructed on the principle of the spinning top of Henriot and Huguenard, the rotor actually having its bearings on a cushion of air. Essentially it consists of (1) a duralumin rotor taking four small tubes, 2 × 0·5 cm.; (2) a phosphor-bronze stator having a series of nine holes drilled obliquely, so as to allow the compressed air to emerge upwards and obliquely upon the grooved rotor; (3) an air-compression plant driven by a 4 h.p. electric motor and delivering 20 cb.ft. of air per minute at a pressure of 80 to 90 lbs. per sq. in. The speed attainable is over 60,000 r.p.m. The frequency of revolution is determined by a stroboscope consisting of a neon light worked at known frequency and controlled by an electrically driven tuning fork.

The determination of the size of the particles is carried out by plotting logarithms of the initial and final concentrations (C_0 and C_T) against time. The straight line obtained by joining C_0 and C_T makes the angle θ with the horizontal; this is called the angle of sedimentation, and it is a function of the velocity of sedimentation of the particles such that their mean diameter $D = K \times \sqrt{\tan \theta}$, where K is a constant varying with the speed of the centrifuge. K was evaluated by conducting a test with staphylococci of known mean diameter (0·8μ), and was found to be 268·3 at 10,000 r.p.m. and 67·08 at 40,000 r.p.m. In this way the mean sizes of many viruses were determined, and the results agreed closely with those obtained by ultra-filtration. With the viruses of vaccinia and pleuropneumonia the angle of sedimentation decreases with increased time of spinning, indicating more than normal variation in the size of particles. D. R. W.

Toxicological and Forensic

Distribution of Veronal among the Organs in a Case of Fatal Veronal Poisoning. J. F. Reith. (*Pharm. Weekblad*, 1937, **74**, 649–652.)—The body, which was that of a suicide, was dissected 2 days after death, and the organs were stored for 50 days in a refrigerator, after which they were examined by the method of Van Itallie and Steenhauer (ANALYST, 1921, **46**, 413). The following results show the amounts (in g.) of material used (*a*), and of veronal found (in mg.) (*b*), respectively, for the various organs:—(1) *Unabsorbed veronal*:—Large intestine, (*a*) 187, (*b*) 210; small intestine, (*a*) 250, (*b*) 300; duodenum, (*a*) 18, (*b*) 260; stomach, (*a*) 105, (*b*) 4750. If the first three results are doubled and added to the fourth, a total of 6290 mg. of unabsorbed veronal is obtained. (2) *Absorbed veronal*:—Urine, (*a*) 45, (*b*) 40; gall, (*a*) 3, (*b*) 20; brain, (*a*) 1200 (estimated), (*b*) 500; liver, (*a*) 1285, (*b*) 1020; spleen and 1 kidney, (*a*) 380, (*b*) 270; blood (contents of right chamber and *vena cava* mixed), (*a*) 6000 (estimated), (*b*) 2420. The total absorbed veronal was therefore 4270 mg., making a grand total of 10·56 g.; the fatal dose for an adult is given as 8 to 10 g. The results are compared with those of Van

Itallie and Steenhauer (*loc. cit.*), and stress is laid on the importance of an examination of all the organs and body fluids if it is desired to obtain accurate information whether the dose taken was sufficient to produce fatal results. J. G.

Determination of Alcohol in Blood, Post-Mortem. E. Kohn-Abrest and L. Truffert. (*Ann. Falsificat.*, 1937, **30**, 210–216.)—Methods such as those of Nicloux (*Bull. Soc. Chim. Biol.*, 1931, **13**, 857; 1934, **16**, 1314; 1936, **18**, 318) and Wilmark (*Biochem. Z.*, 1922, **131**, 473), depending upon the reduction of chromic acid, are excellent for determining alcohol in small amounts of fresh blood taken from the living subject, but have the disadvantage that, if the blood is decomposed, it is not certain that alcohol is the only volatile reducing agent present. The method here described, in which the alcohol is isolated, is applicable when relatively large amounts of blood are available and is valuable in forensic practice when the subject has been fatally injured, and the possibility of alcoholic intoxication is involved. By a series of distillations of blood or viscera the alcohol is obtained as an aqueous solution, and from this it is separated by the addition of anhydrous potassium carbonate. Coniver (*Thèse de la Faculté des Sciences de Dijon*, 1931) and Olszewski (*Travaux du Laboratoire de Toxicologie de la Préfecture de Police*, 1932) have shown that, unless the amount of alcohol is very small and the material is in an advanced stage of putrefaction, the supernatant layer thus obtained represents, with reasonable accuracy, the volume of alcohol present. For viscera the procedure is as follows:—The minced viscera (1000 g.) are distilled with 1 litre of water and 10 g. of tartaric acid, and 700 ml. of distillate are collected. A sixth part of the distillate is reserved for the detection of chloroform, alkyl halides, etc., and the remainder is re-distilled, 170 ml. of distillate being collected. Concentration is continued in the same manner, the volumes of the successive distillates collected being 60 ml., 25 ml. and 10 ml., and a proportionately smaller apparatus (which should be provided with a fractionating column) is used for each distillation. The final concentrate of 10 ml. is divided into two portions, one of which is examined for volatile poisons and the other for alcohol by the method described later. For blood the procedure is as follows:—One hundred ml. (or 50 ml. if the alcohol-content is high) of heart or pulmonary blood (preferably the former) are distilled with 250 ml. of saturated picric acid solution and 50 ml. of water in an apparatus made entirely of glass. To the distillate (150 ml.) 10 ml. of 10 per cent. sodium carbonate solution are added, and the mixture is distilled in a smaller apparatus, 80 ml. of distillate being collected. This, in turn, is reduced to a volume of 40 ml. The successive concentrations are then as follows, the figures in brackets denoting the size of the distillation flask from which the distillate should be obtained:—25 ml. (100 ml.), 12 ml. (75 ml.), 6 ml. (40 ml.), 5 ml. (25 ml.), 2·5 ml. (15 ml.). When the 40-ml. distillate has been collected the graduated receiver is rinsed into the next distillation flask with 10 ml. of water and replaced by a smaller one. Similarly, after the 6-ml. distillate has been collected, the receiver is rinsed with 4 ml. of water and replaced by a still smaller one. The eighth concentrate (2·5 ml.) is placed in a special flask of 5 to 6 ml. capacity, the lower part of which is elongated into a narrow tube graduated in 1/100th ml. and, by means of a suitable funnel, 3 g. of anhydrous potassium carbonate and a trace of solid phenolphthalein are added. The vessel is then filled with saturated potassium carbonate solution, stoppered and placed vertically with the graduated portion upwards. The alcohol, coloured red by the phenolphthalein, collects above the colourless aqueous layer and, when separation is complete, its volume is read and 0·02 ml. is added as a correction. The presence of phenolphthalein is essential when the alcohol-content is low and separation is consequently slow. Copper sulphate may be used instead of phenolphthalein, the alcohol layer then being colourless and the aqueous layer blue. The precision of the method has been verified by determining known amounts of alcohol in decomposed blood. By using 100 ml. of blood 0·4 part of alcohol per thousand can be determined. Pig's blood, kept in a closed vessel for 9 days at 18° to 22° C., gave no trace of alcohol. Viscera that had been kept in ice for two months before analysis gave 3·6 parts per thousand by vol. of reducing substances, expressed as alcohol, and 2·0 parts of alcohol separated by this method. The blood was then kept at room temperature for another month, after which it was found to contain 0·9 part of alcohol per thousand. The tendency, therefore, is for alcohol to disappear as putrefaction proceeds. A. O. J.

Water

Use of Activated Carbon in the Determination of Nitrate, Nitrite and Ammonia in Water and Sewage. G. Gad. (*Gas- u. Wasserfach*, 1936, **79**, 166; *Dept. Sci. Ind. Research—Water Pollution Res., Abstracts*, 1937, **10**, 15).—Activated carbon adsorbs nitrates and nitrites from acid, neutral and weakly alkaline solutions (*p*H 4·5 to 7·4), but not from more alkaline solutions (*p*H 8·5). It may therefore be used for removing turbidity and colour from water and sewage in which nitrate and nitrite are to be determined, provided that the sample is distinctly alkaline. The carbon should be purified by boiling with soda lye, washing with water and dilute hydrochloric acid, and drying. The water under examination should be made alkaline with sodium hydroxide (about 0·1 g. per 100 ml.) before being shaken with the carbon. Purified activated carbon may also be used for removing colour and turbidity (also hydrogen sulphide) from water in which ammonia is to be determined with Nessler's reagent. The sample is acidified with sulphuric or nitric acid, shaken with the carbon and filtered. Colour and turbidity cannot be sufficiently reduced by addition of cadmium acetate alone.

Agricultural

Distinction of Derris and *Lonchocarpus* Powders. A. Diakonoff. (*Pharm. Weekblad*, 1937, **74**, 901–909.)—The ground root of *Lonchocarpus* (cubé or barbasco) sometimes occurs in derris sold as an insecticide, and as the rotenone-content of the matter soluble in ether indicates that the insecticidal power of the latter is 1·5 to 2 times greater than that of the former, such mixtures must be regarded as instances of adulteration. The microscopical characteristics, as observed after clearing in the usual way with chloral hydrate, are described, but they do not afford a trustworthy method of distinguishing between the two powders; the differences in colour and odour are also of no assistance where mixtures are concerned. It is preferable to mount the specimen in water, when the granules of derris are distinguishable by their irregular (usually angular) shape and relatively small size; 3 or more angles are usually visible, and aggregates of 3 or 4 granules frequently occur and give the impression of a composite triangle or square. A small hilum, with 3 or 4 fine branches radiating from a single point, is frequently present. *Lonchocarpus* granules, on the other hand, are much larger and are usually circular or egg-shaped and regular in contour; they may also occur in groups (usually in pairs), and the granules then join along a flattened side, and so still preserve the appearance of a circle. The larger granules usually have a hilum which appears, as a rule, as a single irregular semi-circular line following the contour of the circumference of the granule; the radiating type of hilum also occurs occasionally. These characteristics are illustrated in the original paper. The following results for (*a*) derris and (*b*) *Lonchocarpus* were obtained by plotting the frequency curves of the sizes of the granules:—Number of measurements made, (*a*) 1063, (*b*) 1169; maximum and minimum sizes, (*a*) 2 to 17μ, (*b*) 3 to 28μ; mean sizes, (*a*) 6·38 ± 0·1μ, (*b*) 9·80 ± 0·2μ; mean error of a single determination, (*a*) 2·24, (*b*) 3·70μ; median, (*a*) 5·43, (*b*) 9·50μ. J. G.

Organic

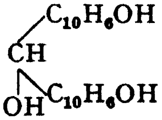
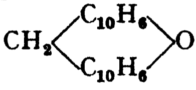
Selectivity of Iodic Acid in the Oxidation of Organic Compounds. R. J. Williams and M. A. Woods. (*J. Amer. Chem. Soc.*, 1937, **59**, 1408–1409.)—A search has been made for oxidising agents that might be sufficiently selective in action to make "partial oxidation equivalent analysis" (*J. Amer. Chem. Soc.*, 1937, **59**, 288, 291, 293) a useful method for determining structure, in that the determination of the amount of reagent used would yield definite information without isolation of oxidation products. Such selective oxidation is effected by treating 5 to 6 mg. of the organic compound with 10 ml. of a 1 per cent. solution of potassium iodate in 40 per cent. sulphuric acid and 2 ml. of water. The mixture is kept at 100° C. for 1½ hours, after which the liberated iodine is removed by steaming, and the unused iodate is determined by titration. When no visible iodine is liberated a titration gives the same results as a blank determination. All compounds obviously oxidised consumed at least 4 milli-equivalents of oxidising agent per millimole. The simple aliphatic alcohols tested (up to octyl alcohol) were oxidised except methanol, which was not oxidised in a sealed tube; polyhydric alcohols, such as glycol, glycerol, mannitol, inositol, etc., were not oxidised, but when the alcohol contained an unoxidised carbon atom in the alpha position to a hydroxyl group, as in trimethylene glycol, pinacol and propylene glycol, oxidation occurred. All the aliphatic and aromatic aldehydes tested were oxidised, as were also acetone, methyl-ethyl-ketone and acetophenone, but not benzophenone or benzil. Simple fatty acids (including formic acid) and aromatic acids gave negative results, as also did glycollic, lactic, tartaric, citric, mucic, mandelic and benzilic acids, and the unsaturated maleic and crotonic acids. Amino acids of protein origin (16 samples) were unoxidised, with the exception of cystine, tyrosine and tryptophane. All the aldohexoses and their derivatives tested gave negative results; a slight oxidation of cellobiose and trehalose was attributed to impurity.

Fructose, sorbose and sucrose were oxidised (the last-named probably owing to fructose formation), but benzoin was unaffected. The pentoses, *d*-arabinose and *l*-xylose (rhamnose more slowly) were oxidised, presumably owing to the formation of furfural. All the phenolic compounds tested (13), the phenol ethers, anisole and phenetole, and the 7 aniline derivatives tested were oxidised. D. G. H.

Use of Leucobases as Analytical Reagents. A. I. Matiu and C. Popesco. (*Bull. Soc. Chim.*, 1937, **4**, 1230–1235.)—The leucobase of methylene blue is oxidised in the air, but can be stabilised by forming the sulphone. An analytical reagent was made by treating 10 ml. of 0·1 per cent. aqueous methylene blue solution with 10 drops of 12 per cent. sodium thiosulphate solution and 20 drops of 1 per cent. hydrochloric acid. When shaken and allowed to stand for 5 to 15 minutes the mixture was completely decolorised. This thiosulphone reagent is stable in air for about 12 hours; strips of filter paper impregnated with it and dried in the dark are stable for about 24 hours. It can be used to distinguish oxidising from neutral or reducing media, giving a blue colour with oxidising solutions. Pancreatin gave a green-blue colour and a green precipitate, but pepsin, tyrosinase and yeast did not react. Most neutral inorganic salts are inactive, except those that have an oxidising action; with fixed alkalis, ammonia, potassium ferro- and ferricyanides, a blue colour is obtained; most reducing salts (sodium nitrite and hypophosphite are exceptions) are inert. E. M. P.

Detection of the Nitro Group in Organic Compounds. W. M. Hearon and R. G. Gustavson. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 352–353.)—A semi-micro test for the detection of nitro groups in organic compounds is based on the oxidation of ferrous to ferric hydroxide. The solutions required are:—(A) A solution of 25 g. of ferrous ammonium sulphate in 500 ml. of air-free water and 2 ml. of conc. sulphuric acid, and (B) alcoholic potassium hydroxide solution. Thirty g. of potassium hydroxide, dissolved in 30 ml. of water, are added to 200 ml. of 95 per cent. alcohol. *Method.*—Ten mg. of the finely-powdered organic substance are added to 0·7 ml. of (A) in a 4-ml. test-tube. After the addition of 0·5 ml. of (B) air is removed by means of a stream of inert gas, and the tube is quickly stoppered and shaken. In test analyses, all aromatic nitro compounds examined gave a brown precipitate in less than 30 seconds. Nitromethane, the only aliphatic compound tested, required 60 seconds. The reaction is not specific, but is also obtained with nitroso compounds, aliphatic nitrates and nitrites, quinones, and hydroxylamine. With these exceptions, seventy-five compounds not containing the nitro group gave negative results; many of them produced a light green precipitate, which in some instances became dark, owing to slight oxidation. Thus, when correlated with other tests, the reaction should be useful. It fails with highly coloured compounds. E. B. D.

Reactions between Formaldehyde and Naphthols. A. Castiglioni. (*Gazz. Chim. Ital.*, 1937, **67**, 324–326.)—When heated on the water-bath in the presence of conc. hydrochloric acid both α- and β-naphthols condense with formaldehyde to give a precipitate—red-brown with α-naphthol and red with β-naphthol.

On addition of alkali (preferably solid sodium hydroxide) the α-naphthol precipitate becomes azure blue, a reaction that will distinguish small quantities of the two naphthols when the red-brown and red precipitates are too similar in colour to be discriminated. With both naphthols the first condensation product is dinaphtholmethane; with α-naphthol this oxidises to dinaphtholcarbinol  $CH(OH)(C_{10}H_6OH)_2$; with β-naphthol the dinaphtholmethane undergoes intramolecular condensation to give dinaphthopyran,  $CH_2(C_{10}H_6)_2O$, m.p. 185° C. E. M. P.

Determination of Furfural and Methylfurfural in Mixtures. E. E. Hughes and S. F. Acree. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 318–321.)—At a temperature of 0° C. and under the same conditions, methylfurfural reacts more rapidly than furfural with bromine solution. Under the standard conditions of Hughes and Acree (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 123; Abst., ANALYST, 1934, **59**, 430) furfural reacts quantitatively with bromine in equimolecular proportions in 5 minutes, and further change is almost negligible after 1 hour. The rate of reaction of methylfurfural has been studied and the values for molecular consumption of bromine after different periods of time have been calculated. Hence, if duplicate solutions of a mixture of these aldehydes are made to react with equal amounts of bromine for different periods of time and the consumption of bromine by each is determined, the composition of the mixture may be found by means of the following formulae:

$$m = (0{\cdot}055)\,\frac{a_1x_2 - a_2x_1}{a_1b_2 - a_2b_1}$$

$$f = (0{\cdot}048)\,\frac{b_1x_2 - b_2x_1}{a_1b_2 - a_2b_1}$$

where m represents grams of methylfurfural, f grams of furfural, x_1 and x_2 are the total milli-equivalents of bromine consumed after periods t_1 and t_2, and a_1, a_2, b_1, b_2 are the molecular consumptions of bromine by furfural and methylfurfural respectively for the same periods of time. When $t_1 = 5$ minutes and $t_2 = 10$ minutes, $a_1 = a_2 = 1{\cdot}00$, $b_1 = 1{\cdot}38$, and $b_2 = 1{\cdot}63$. The method used is that of Hughes and Acree (*loc. cit.*). Their side-arm titration flask is described in a later paper (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 292; Abst., ANALYST, 1934, **59**, 712); it now has thermometer wells, extending into the solution, attached to each stopper of the flask. The temperature is maintained at 0 to 0·5° C. throughout the determination. The reagents are (i) 25 ml. of $N/10$ potassium bromate solution, containing potassium bromide, (ii) 10 ml. of 10 per cent. potassium iodide solution, (iii) 200 ml. of N hydrochloric acid, in which the sample containing the aldehydes is dissolved. In test analyses the mean error in the results was about 0·5 mg. with samples containing from 3 to 50 mg. of methylfurfural. E. B. D.

Wax-like Constituents of the Cherry, *Prunus avium* L. K. S. Markley and C. E. Sando. (*J. Biol. Chem.*, 1937, **119**, 641–645.)—Solid fatty acids, liquid fatty acids, glycerol and hydrocarbons have been obtained from a petroleum spirit extract of the skins of Bing cherries (*Prunus avium* L.). The solid fatty acids consisted of palmitic, stearic and a small amount of an acid higher than C_{18}; the liquid acids were linolic and oleic, and the hydrocarbons consisted chiefly of nonocosane together with one of a greater chain length. An ethereal extract of the skins yielded α-glucosido-sitosterol and ursolic acid. The yield of the petroleum spirit extract was 0·8 per cent. and that of the ethereal extract 0·1 per cent. of the dried skin. A comparison of these figures with the previously reported yields from apple and pear cuticles, *viz.* apple 3·24 and 4·61 per cent., and pear 1·95 and 2·38 per cent. for the petroleum spirit and following ethereal extracts, respectively (*J. Biol. Chem.*, 1935, **111**, 133; Abst., ANALYST, 1935, **60**, 767), suggests an explanation for the less efficient protective surface coating of the cherry. S. G. S.

Diphenylguanidine as a Standard in Neutralisation Processes. W. M. Thornton and C. L. Christ. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 339.)—In test analyses with diphenylguanidine as an original standard in acidimetry and alkalimetry, Carlton (*J. Amer. Chem. Soc.*, 1922, **44**, 1469–1474; Abst., ANALYST, 1922, **47**, 408), obtained excellent results, but this has not been the experience of other chemists. The authors have titrated diphenylguanidine with approximately *N*/10 hydrochloric acid, using Carlton's double indicator (bromophenol blue and methyl red), which gave a sharp end-point. The mean factor in four titrations was 0·10114 *N*. The acid had been prepared by diluting a measured amount of hydrochloric acid of constant b.p. to the required volume, and the factor calculated from this was 0·10058 *N*. Gravimetric analysis, in which the chloride was precipitated with silver nitrate, gave factors of 0·10054 *N* and 0·10049 *N*. The diphenylguanidine had been purified by Carlton's method (*loc. cit.*). Further research is being carried out on the preparation of pure diphenylguanidine and also of triphenylguanidine (*cf.* Callan and Strafford, *J. Soc. Chem. Ind.*, 1924, **43**, 1T). E. B. D.

Inorganic

Determination of Cadmium in Tin-rich Alloys by Loss in Weight. D. Hanson and W. T. Pell-Walpole. (*Tech. Publ. Internat. Tin Research and Dev. Council*, Series A, No. 55, 1937.)—Volatilisation of cadmium from alloys rich in tin can be made so complete without appreciable loss of tin that it is proposed as a method of analysis. A 3-g. sample of the alloy in a porcelain boat is placed in a silica tube closed at one end and connected with a vacuum pump at the other end. The tube is heated at 700° to 730° C. for 30 minutes. A high vacuum in the tube is unnecessary, reduction of pressure to 1 mm. of mercury having been found satisfactory. The evacuated tube is removed from the furnace and allowed to cool below the melting-point temperature of tin before air is admitted. The sample is then removed and weighed when cold, the loss in weight being taken as the cadmium-content. Results very close to the intended composition were obtained with (*a*) binary alloys containing 0·25 to 50·0 per cent. of cadmium in tin and (*b*) ternary alloys containing similar amounts of cadmium in tin with 2 to 14 per cent. of antimony. Neither pure tin nor tin alloyed with 14 per cent. of antimony was found to lose weight under the above-mentioned conditions. S. G. C.

Determination of Arsenic in Tin. B. Tougarinoff. (*Bull. Soc. Chim. Belg.*, 1937, **46**, 141–170.)—A detailed study has been made of the methods for the determination of small quantities of arsenic in refined tin, based either on distillation as arsenic trichloride or evolution of arsine, and described in the literature (Lunge-Berl; *Ausgewählte Methoden*; American Society for Testing Materials; Villavecchia). Both methods were found to give reliable results; in the evolution method a correction of 0·2 to 0·3 mg. has to be made for the quantity of arsenic not volatilised as arsine. W. R. S.

Specific Reagent for the Determination and Separation of Thallium. R. Berg and E. S. Fahrenkamp. (*Z. anal. Chem.*, 1937, **109**, 305–315.)—The reagent is the β-aminonaphthalide of thioglycollic acid, $C_{10}H_7NH.CO.CH_2.SH$, in which the hydrogen atom of the SH-group is replaceable by metals. Precipitation of thallium is specific in alkaline tartrate solution containing cyanide, the complex $Tl(C_{12}H_{10}ONS)$ forming a lemon-yellow, crystalline precipitate containing 48·60 per cent. of thallium. The sulphate solution is neutralised with 2 *N* sodium hydroxide solution, treated with 2 g. of sodium tartrate, 3 to 5 g. of potassium cyanide, and 10 to 20 ml. of 2 *N* sodium hydroxide solution, and diluted to 100 ml. Precipitation is carried out in the cold with 4 to 5 times the theoretical amount of reagent in concentrated acetone solution. The amorphous precipitate becomes crystalline when the solution is stirred and boiled. The vessel is cooled in water, and the liquid is filtered through a porous glass crucible (G4); the precipitate is washed with cold water until free from cyanide and then with acetone to remove excess of reagent, and dried to constant weight at 100° C.

For the separation of thallium from other metals the following solutions are required:—a freshly made 5 per cent. solution of the reagent in acetone (it decomposes after a few hours); sodium tartrate solution, 20 per cent.; potassium cyanide solution, 20 per cent.; 2 *N* sodium hydroxide solution. The thallium solution (100 ml.) is treated with 10 to 25 ml. of tartrate solution and neutralised towards phenolphthalein with the alkali. Sufficient cyanide solution is added to make the final concentration 5 per cent. The alkalinity is then raised to normality by the addition of alkali. Precipitation is effected exactly as described above; the precipitate should not be compressed too strongly by suction, otherwise washing is less effective.

If iron is present, the ferricyanide formed should be reduced to ferrocyanide by means of hydroxylamine. Vanadate should be similarly reduced to vanadyl salt. Uranyl salts are kept in solution by the addition of ammonium carbonate, and by washing the precipitate with 10 per cent. ammonium carbonate solution, followed by water and acetone. In the presence of mercury, bismuth or lead, the thallium should be precipitated with a tenfold excess of reagent dissolved in sufficient acetone to provide a 30 per cent. concentration of the solvent in the final bulk of liquid; mercury also requires 9 g. of cyanide per 100 ml. of final liquor. The carbonates of the alkaline earths, as well as magnesium hydroxide, are insoluble in alkaline cyanide solution, but these elements can be separated from thallium by substituting ammonia for 2 *N* sodium hydroxide in the procedure described. W. R. S.

Gravimetric Determination of Zinc by means of Anthranilic Acid. E. A. Ostroumow. (*Ann. Chim. anal.*, 1937, 19, 173–176.)—Funk and Ditt's method (*Z. anal. Chem.*, 1933, **91**, 332; Abst., ANALYST, 1933, **58**, 241), applied as follows, is recommended. The slightly acid solution of zinc, from which metals other than those of the alkalis or alkaline earths are absent, is made slightly alkaline with sodium hydroxide and then acidified with a few drops of dilute acetic acid. Ammonium acetate should not be present. After dilution of the solution to about 150 to 200 ml. for each 0·1 g. of zinc present, an excess of sodium anthranilate solution is added slowly, with shaking, which is continued for 3 to 5 minutes. The precipitate of zinc anthranilate is filtered off after standing for about 20 minutes, washed first with dilute sodium anthranilate solution and then with alcohol, dried at 105 to 110° C., and weighed; 1 g. of the precipitate corresponds with 0·2411 g. of zinc oxide or 0·1937 g. of zinc. The reagent is prepared by dissolving 3 g. of anthranilic acid in dilute sodium hydroxide solution in amount just insufficient to neutralise the acid, and diluting the liquid to 100 ml. Quantitative results were obtained with pure solutions containing 0·05 g. of zinc. In order to apply the method it is, in general, necessary to effect a preliminary separation of the zinc as sulphide; the zinc sulphide precipitate is converted by heating into zinc oxide, which is dissolved in the minimum quantity of hydrochloric acid. S. G. C.

Sensitive Test for Manganese. E. Jensen. (*Z. anal. Chem.*, 1937, **109**, 178–181.)—The solution to be tested (1 ml.) is mixed with 2 ml. of strong hydrochloric acid and about 4 ml. of a mixture of equal volumes of ether and strong hydrochloric acid. A few small crystals of potassium chlorate added to the solution will give a green colour in a few seconds if manganese is present. The coloured compound is probably manganese trichloride. If less than 0·05 mg. of manganese per 10 ml. is present, the yellow colour of the liberated chlorine will mask the green tint. A more sensitive form of the test is as follows:—A few drops of the original solution are evaporated to dryness in a porcelain capsule. The warm residue is moistened with a few drops of strong nitric acid, cooled and treated with the mixture of ether and hydrochloric acid. This procedure will detect 0·005 mg. of manganese. The colour is stable for one-half to several hours. Metals yielding coloured solutions (nickel, copper, chromium, and especially cobalt) decrease the sensitiveness of the test. W. R. S.

Detection of Selenium. H. A. Ljung. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 328–330.)—When ammonium thiocyanate solution is added to a solution of selenious acid in hydrochloric acid and the mixture is boiled for 1 minute, a red precipitate of metallic selenium is obtained. For complete precipitation at least 4 mols. of ammonium thiocyanate per mol. of selenious acid are required, and the acidity of the selenious solution should be not less than 6 *N* hydrochloric acid. With small quantities of selenium the reaction is complete after 20 to 30 seconds. If the amount of selenium present is very small, the precipitate remains in suspension for a considerable time, and its colour in reflected light varies from red through green and greenish-yellow to almost white as the concentration diminishes. The test is sensitive to 0·05 part of selenium per million in 7 *N* acid thiocyanate solution. If the mixture is allowed to stand for 48 hours after heating, the sensitivity is 1 part of selenium in 38 millions of 7 *N* hydrochloric acid solution. Ferrous, antimonious, and stannous ions interfere with the reaction. Attempts are being made to base a quantitative method on this reaction. E. B. D.

Determination of the Acids of Selenium and Arsenic in Presence of Each Other. J. Milbauer. (*Z. anal. Chem.*, 1937, **109**, 171–177.)—The following process was worked out for the determination of arsenate, arsenite, selenate and selenite in one and the same solution. (1) *Arsenate* is determined in the usual manner by precipitation with magnesia mixture. (2) *Arsenite* must be determined indirectly, by oxidation with ammoniacal hydrogen peroxide followed by precipitation with magnesia mixture, the excess of arsenic over that found under (1) being calculated to arsenite. (3) *Selenate* is precipitated as barium selenate in presence of perchloric acid. The solution is slightly acidified with 10 per cent. perchloric acid, treated with 2 drops of 10 per cent. silver perchlorate solution, heated to boiling, and stirred while being precipitated with 0·5 to 0·25*M* barium perchlorate solution added drop by drop. The precipitate is left to settle on the water-bath, collected next day in a porous porcelain crucible (A1 or A2) by means of its mother-liquor, and washed 4 times with portions of not more than 2 to 3 ml. of cold water. The barium selenate is dried to constant weight at 105° C. (4) *Selenite*, like arsenite, must be determined by an indirect procedure. This consists in reducing selenate and selenite to the element, calculating the selenate found under (3) into selenium, and the excess of selenium into selenite. A fresh aliquot portion of the original solution is acidified with 10 to 15 ml. of hydrochloric acid, diluted (300 to 400 ml.), treated with hydrazine sulphate, and gradually warmed on the water-bath. The reduction should be gradual, since otherwise the precipitate becomes contaminated with arsenic, as is shown by its collecting in voluminous dark flocks. Heating is continued until the selenium has deposited as a dark grey powder. This is collected in a porous porcelain crucible, washed with hot water and dried at 105° C. to constant weight. Molybdate mixture can only be used for concentrating traces of arsenic acid; the yellow precipitate is strongly contaminated with selenium compounds; these can be eliminated by precipitation of the arsenic acid with magnesia mixture. W. R. S.

Precipitation of Vanadates. E. Carrière and H. Guiter. (*Compt. rend.*, 1937, **204**, 1339–1340.)—A number of statements are made concerning the precipitation of metallic vanadates at different *p*H values. The addition of barium chloride to solutions containing the ammonium or sodium salts of vanadic acid, at *p*H 3·5 to 4·5, precipitates barium metavanadate $Ba(VO_3)_2$, the solubility of which is not sufficiently low to make it a useful precipitation form for gravimetric analysis. At *p*H values between 4·5 and 10·8 a precipitate is produced having the composition $(BaO)_x(V_2O_5)$, where *x* varies between 1 and 3. The authors were unable to obtain a stage corresponding with the precipitation of barium pyrovanadate; thus Carnot's method, which is based on the precipitation of barium pyrovanate, did not appear capable of giving very accurate results. Between *p*H 10·8 and 11·4 barium orthovanadate is precipitated quantitatively, but has the drawback of being contaminated with barium carbonate, which also readily precipitates within this *p*H range. Silver metavanadate is precipitated from a solution containing acetic acid at *p*H 4 to 4·6. Lead orthovanadate, $Pb_3(VO_4)_2$, is precipitated from acetate solution at *p*H 4·3 to 5. The gravimetric determination of vanadates as lead vanadate is more accurate than as silver vanadate. S. G. C.

Microchemical

Microscopic Tests for Amino Acids. J. D. Surmatis and M. L. Willard. (*Mikrochem.*, 1937, **21**, 167–171.)—Amino acids react with reagents for alkaloids and solutions of salts of the heavy metals, frequently forming characteristic crystals which can be examined with a petrological microscope at 250×. For the tests a few crystals (less than 5 mg.) of the amino acid are dissolved in 20 per cent. hydrochloric acid, and the solution is neutralised with ammonium hydroxide (faint pink with phenolphthalein). Drops of the solution are treated with 10 per cent. solutions of the reagents on microscope slides. A precipitate is not formed immediately, but, as a rule, crystals appear on allowing the liquid to dry slowly. Nine specific tests are recorded for tyrosine and one for glycine (with Millon's reagent). Comparative tests were applied to glycine, cystine, tyrosine, alanine, glutamic acid, aspartic acid, leucine, phenylalanine and proline. The following reagents were tried: barium hydroxide, copper nitrate, lead acetate, magnesium hydroxide (results poor), Marmé's reagent, Mayer's reagent, mercuric chloride (only fair results), Millon's reagent, picric acid, picrolonic acid, platinic chloride (only fair results), potassium iodate, saccharin, silicotungstic acid, sodium nitroprusside (only fair results), tannic acid (only fair results), Wagner's reagent (only fair results), zinc hydroxide. Sixteen photomicrographs are given. J. W. M.

Microscopy of the Amino Acids and their Compounds. III. Copper Salts. B. Cunningham, M. MacIntyre and P. L. Kirk. (*Mikrochem.*, 1937, **21**, 245–247.)—The copper salts were prepared on the microscope slide by addition of solid cupric acetate to drops of solutions of the amino acids. Usually it was sufficient to prepare a saturated solution of the amino acid at room temperature. Many acids form more than one variety of crystals; generally two or more different forms appear in the same preparation, owing to local variation in conditions. In every instance the optical properties of one variety were investigated. The following form crystalline copper salts suitable for optical examination:—alanine, aspartic acid, cystine, glycine, isoleucine, leucine, lysine, methionine, nor-leucine, nor-valine, phenylalanine, serine, valine and α-amino-*n*-valeric acid. Most of these salts crystallised in thin bluish plates; a few formed needles. Sixteen photomicrographs are given. J. W. M.

Microchemical Reactions for Identifying Tellurium. G. Denigès. (*Compt. rend.*, 1937, **204**, 1256–1258.)—*Reaction with bromine.*—Minute particles (a fraction of a mg.) of the metalloid to be identified are placed on a glass slide and covered with two drops of a 20 per cent. solution of bromine in chloroform. When the liquid has spontaneously evaporated a yellow residue is left. This should appear quite dry. If it appears damp, the slide is warmed somewhat by passing it through the flame of a Bunsen burner and then allowing it to cool. One drop of a 2 : 1 mixture of chloroform and 95 per cent. alcohol is added, and the slide is placed on a surface heated to 35° to 40° C. in order to remove the solvents by evaporation. The residue is examined microscopically (×150 to 300). Tellurium is shown by the presence of a large number of more or less clear yellow hexahedral or octahedral crystals (sensitiveness of test: 0·05 mg.). *Reaction with iodine.*—To some particles (a fraction of a mg.) of the substance on a glass slide are added 3 or 4 drops of a 10 per cent. solution of iodine in alcohol (without potassium iodide). The drops are made to spread somewhat by manipulating the slide held in the hand. After about 1 minute, when the liquid has evaporated to a syrupy consistence, the slide is gently heated over a Bunsen flame in order to drive off most of the iodine. After cooling, the dry residue is examined microscopically (×150 to 300). Tellurium is shown by collections of small black crystals of tellurium iodide. These are soluble in alcohol and acetone, but insoluble in carbon tetrachloride. The halide compounds of tellurium are decomposed by ammonia, sodium hydroxide solution and dilute sulphuric and hydrochloric acids, giving solutions from which elemental tellurium can be precipitated by reducing agents.

S. G. C.

Microchemical References, 1936. (Supplement to *Mikrochem.*, 1936–37, **21**, 1–76.)—References are given in alphabetical order of the authors' names under the following headings. I. *Pure microchemistry*: (1) general and apparatus, 9 pages; (2) inorganic analysis, 8 pages; (3) organic analysis, 4 pages; (4) preparative, 1 page; (5) physical chemistry, 8 pages. II. *Applied microchemistry*: (1) biological chemistry, 9 pages; (2) medical and pharmaceutical chemistry, 8 pages; (3) mineralogical chemistry, 4 pages; (4) technical chemistry, 16 pages. Additions to previous volumes of microchemical references, 1931–1935, under the same headings, cover 27 pages; both the original reference and those of abstracts are given.

J. W. M.

Collected References. Micro-determination of Potassium. Ch. Cimerman and C. J. Rzymowska. (*Mikrochem.*, 1936, **20**, 129–143.) The 83 references include work published between 1929 and March, 1935, as references prior to 1929 have already been collected (*cf.* Heller, Haurowitz and Stary, "Alkali Metals," *Mikrochem.*, 1930, **8**, 182). The methods are described under the following headings:—Determination with (1) sodium cobaltihexanitrite, (2) chloroplatinic acid, (3) perchloric acid, (4) perrhenic acid, (5) zirconium sulphate, (6) tartaric acid, (7) organic reagents, (8) physico-chemical methods. The cobaltinitrite method (42 references), whether applied gravimetrically, volumetrically or colorimetrically, is the most recommended. Various authors give the error of the gravimetric method as 1 per cent.; filter sticks or Jena glass filters are used for the filtration. The error of the method used colorimetrically is about 2 to 3 per cent.; this procedure is most suitable for rapid analysis and biological work. The platinic chloride method (8 references) may also be applied gravimetrically, volumetrically or colorimetrically. In the presence of large amounts of sodium it is best to precipitate the potassium first as the perchlorate or cobaltinitrite, and then to dissolve and re-precipitate it as the chloroplatinate. Errors may arise in washing the precipitate with alcohol containing a trace of aldehyde, which may cause a partial reduction of the compound. The perchlorate method (6 references) is less suited to microchemical work, owing to the solubility of the compound and its relatively small molecular weight; the perrhenic acid method is similar (2 references) and preferable because of the higher molecular weight of the reagent which, however, is rare and expensive. The zirconium sulphate method (2 references) is held to be as accurate as the perchlorate method; it may be applied nephelometrically. J. W. M.

Physical Methods, Apparatus, etc.

Sensitive Method for the Detection of Traces of Rare Earth Elements. M. Servigne. (*Compt. rend.*, 1937, **204**, 863–865.)—The method is an application of the results of the author's previous study of luminescence (*id.*, 1936, **203**, 1247). The finely divided substance is intimately mixed with a diluent, such as calcium tungstate, and sealed into a glass ampoule containing rarified gas and mercury vapour. Luminescence is brought about by exciting the interior of the ampoule with an electric discharge. The principle of the detection consists in the examination of the photo-luminescence spectrum, photographed on a panchromatic plate, for the principal rays of the element in question. It is stated that in this way it is possible to detect as little as 10^{-5} to 10^{-7} g. of elements such as samarium, dysprosium and europium in 1 g. of the mixture. Owing to the large surface exposed by the grains of the mixture, the sensitiveness of the method is much greater than that of an alternative photo-luminescence method in which the substance to be tested is dissolved in a small borax bead. S. G. C.

Micro-determination of Samarium by a Photo-luminescence Method. M. Servigne and E. Vassy. (*Compt. rend.*, 1937, **204**, 1566.)—The qualitative method referred to in the preceding abstract has been extended to give quantitative results, the principle being to compare the intensities of the same samarium emission band given by the sample and by a series of standards containing known amounts of samarium. Quantities of the order of 10^{-4} to 10^{-5} g. of the element can be determined, with an accuracy of 5 per cent. For details of the precautions required to ensure uniformity in working and of the technique required for the photometry of the spectra, the original paper should be consulted. S. G. C.

Spectrophotometric Determination of the Colour of Wine. A. Boutaric, L. Ferre and M. Roy. (*Ann. Falsificat.*, 1937, **30**, 196–209.)—To obtain reliable measurements of the colour of wine by the spectrophotometer, it was found necessary to use cells of less than 1 cm. in thickness, the actual thickness being measured to within 1/100th mm. The optical density $h = \text{Log}_{10}\text{I}_0/\text{I}$ is then calculated to a standard cell-thickness of 1 cm. For all the wines investigated, the absorption curves exhibited maximum values in the region of 520$m\mu$ and, since this is the region to which the human eye is most sensitive, the optical density is a measure of the opacity of the wine. The ratio of the optical density h_1 at 480$m\mu$ to the optical density h_2 at 640$m\mu$, serves as a useful measure of the colour of the wine, h_1 being a measure of the opacity to blue light and h_2 of the opacity to red light. To prevent deposition of the colouring matter in the investigation of the effect of dilution upon colour, the diluent used was an aqueous, 15 per cent. by volume, solution of alcohol. According to Beer's Law, if n is the coefficient of dilution (*i.e.* the volume containing 1 ml. of the original wine) and h the optical density, the product nh, should be constant for a given wine. It was found that, for all wave-lengths, the value of nh diminishes in a non-linear manner, at first rapidly and then more slowly, as n increases. On diluting the wine with water and determining the optical density rapidly before the colouring matter separated, slightly different results were obtained, but these, again, were in disagreement with Beer's Law. A solution in 50 per cent. alcohol, of the colouring matter of the grapes from which one of the wines (Oberlin) was prepared, was found to obey Beer's Law. The explanation suggested is that, in the latter solution, the colouring matter exists in the form of simple molecules which are not greatly altered by dilution, whereas in the wine, the colour exists as complex micelles in equilibrium with the other constituents. When equilibrium is disturbed by dilution, the micelles break down into simpler bodies. It is generally assumed that the colour of a mixed wine may be calculated from the colours of its components by application of the mixture rule. Experiments showed, however, that this is only approximately true, the deviation from the rule being small for wave-lengths of 640$m\mu$ and 480$m\mu$, but considerable at 520$m\mu$, the region of the characteristic colour of wine. To determine the effect of neutralisation upon the colour of wine, the *p*H and absorption curves were determined for samples of wines to which increasing amounts of sodium hydroxide solution had been added. The results show that, proportionally as the *p*H increases, (1) a minimum appears in the absorption curve at 480$m\mu$ and at the same time the maximum is displaced towards the red, and (2) the ratio h_1/h_2 of the optical densities for the wave-lengths 480$m\mu$ and 640$m\mu$ diminishes, showing that the transmitted light becomes increasingly richer in light of short wave-length. A. O. J.

Amorphous Part of Starch in Fresh Bread and in Fresh Pastes and Solutions of Starch. J. R. Katz. (*Rec. Trav. Chim. Pays-Bas*, 1937, **56**, 785–793.)—The *X*-ray spectrogram of the white precipitate formed by dehydration of a 5 to 10 per cent. starch paste by rapid addition of a 20-fold quantity of 96 per cent. alcohol, is known as the "V-pattern" (*cf.* J. R. Katz and A. Weidinger, *id.*, 1934, **53**, 949). It is now considered to be the result of the superimposition of the amorphous pattern of starch and a purely crystalline V-pattern. If this is correct, the change in the starch during the staling of bread may be explained as being due to the crystallisation of the amorphous portion of the swollen granules. The micelles in fresh dilute starch paste or solutions are, therefore, mainly amorphous, whilst in concentrated pastes or solutions they may be partly crystalline and will therefore produce a V-pattern. These spectrograms also indicate that a compound of starch and alkali is present in starch pastes which have been gelatinised by alkali at room temperature, and then rapidly precipitated with alcohol. If the alkali is subsequently removed by washing thoroughly with acid, a V-pattern is obtained, indicating that the above-mentioned compound has been split up. An analogy between these phenomena and the mercerisation of cellulose may be traced (*cf. Z. physik. Chem.*, A., 1930, **150**, 37, 60, 81). J. G.

Efficient Fractionation Equipment for the Qualitative and Quantitative Examination of Natural Fats. H. E. Longenecker. (*J. Soc. Chem. Ind.*, 1937, **56**, 199–202T.)—In order to effect the maximum separation of ester mixtures, an electrically-heated packed column has been devised, in which the rate of distillation can be adjusted. The Pyrex column, which is 90 cm. high and 17 mm. in internal diameter, is packed with single-turn glass helices for a length of 60 cm. It is heated by 15 ft. of nichrome wire (No. 22) wound on a piece of 25-mm. Pyrex tubing for the length of the packed distance, and the heating jacket is insulated by a Pyrex tube, 33 mm. in diameter. The temperature of the column, recorded by a thermometer inserted between the column and heated jacket, is controlled by external fixed and variable resistances. The still-head at the top of the column encloses a thermometer, and collection of the distillate is regulated by a stop-cock (2 mm.) below the condenser, with a separate connection for maintenance of low pressures or release of pressure when the stop-cock is closed. Except towards the end of distillation, the temperature of the vapour at the top of the column should approximate to that of the b.p. of the material being collected, and should be an index of the efficiency of fractionation. The temperature rise for adjacent members of the fatty acid series is about 15° to 20° C., according to the pressure (0·1 to 2 mm.). Maximum efficiency is obtained by so regulating the bath and column temperatures that there is never a visible accumulation of liquid in the packed length of the column. The stop-cock is kept closed at first and at frequent intervals during the collection of intermediate fractions, to enable equilibrium between liquid and vapour phases to be attained. A normal ester mixture obtained in the analysis of a relatively simple fat may be effectively separated when distilled at the rate of 20 to 25 g. per hour. Several sets of typical distillation data, including analyses of "solid" esters of beef tallow and butter-fat "liquid" esters, are given, and the use of the column for the qualitative and quantitative determination of minor components in natural fats is suggested. Thus the occurrence of small amounts of palmitoleic and myristic acids in arachis oil has been demonstrated. The fact that concordant results were obtained in the composite analysis of arachis oil by the use of this column and of a Willstätter bulb is interpreted as an indication of the general accuracy of ester fractionation procedure in the analysis of natural fats.

D. G. H.

Reviews

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS. By I. M. KOLTHOFF and E. B. SANDELL. Pp. 749. New York: The Macmillan Co. 1936. Price 20s.

This new work strikes one as a cross between two more usual types—one the book on practical analytical processes, and the other the book dealing with theoretical fundamentals and physico-chemical interpretation. The present book shows some of the best features of both, and is thoroughly up-to-date. One gets the impression at first that over-much space is taken up with the theoretical aspects, but in reality the treatment is well balanced, for it is divided evenly between the fundamental theories of the subject, the practical methods of working and the more important methods of analysis. The authors maintain that the important end is to familiarise the student with the procedures of analysis, and to awaken a sense of proportion in his work. For example, in an excellent chapter on errors in quantitative analysis (pp. 250–278), it is stated: "Obviously it is a waste of time and labour to determine a constituent with great accuracy, even when this is possible, if there is no particular demand for a very accurate result . . . it is all a matter of commonsense; the analyst must possess a sense of values." However, for the most part, special attention is paid to procedures capable of giving high accuracy. "The analyst who can perform accurate analyses and who has a grasp of the factors involved . . . will understand what legitimate changes can be made in a procedure when results of lesser accuracy are satisfactory."

The book is divided into four chief sections: gravimetric analysis (about 400 pages), volumetric analysis (about 200 pages), physico-chemical methods (about 45 pages), and the analysis of complex materials (brass, steel, silicate rocks, about 60 pages). The first two sections are subdivided into theoretical and practical parts. The theoretical matters are discussed to quite an advanced stage, usually with reference to so-called typical examples. As a result of a discussion of the factors affecting the formation and properties of precipitates, the interesting conclusion is reached that the purest precipitate can often be obtained in the following way: "The precipitation is made at room temperature from concentrated solution; the suspension is diluted with water, or, better, with an electrolyte solution in which the precipitate is more soluble than in water (to promote speed of recrystallisation) and is digested overnight on a steam-bath." The situation, however, is so complex that this conclusion cannot be put indiscriminately into practical effect. In fact, when the authors come to describe precipitation methods, the more usual method of precipitating in a hot solution is frequently given, even for precipitates such as calcium oxalate, barium sulphate, and the like, for which it might be thought that the conclusion quoted above was readily applicable.

In the practical part, full descriptions of selected methods are given for a limited number of elements. There are useful examples in which the relative advantages of a classical method and a more modern method are contrasted, as, for instance, the hydroxide and the hydroxyquinoline methods for aluminium. The book does not set out to be encyclopaedic, although where a full description is not given for the determination of a particular element, various methods are often briefly outlined or indicated by a literature reference. This system results in some elements not being dealt with very adequately—tin, for example; antimony is only mentioned in passing as being determined by potassium bromate, no directions being given. In the volumetric part many instances occur of the use of the newer adsorption and oxidation-reduction indicators, standard ceric sulphate solution, and so on.

The numerous recent literature references add to the value of the book, but it was observed that British work is not very well represented. Among some minor slips is a statement (p. 496), made in connection with calibration of volumetric glassware, that 15° C. is the standard temperature for calibration in England, whereas the B.S.I. have for some time past adopted 20° C.; this, however, does not affect the usefulness of the calibration table given, since this is based on a standard temperature of 20° C., the temperature used in the United States. It is implied (p. 545) that zinc can be determined in the same way as nickel by cyanide—silver nitrate titration; this would not appear to be correct in view of the ready dissociation of the zinc-cyanide complex compared with the nickel-cyanide complex. The statement (p. 606) that quadrivalent tin is reduced by metallic iron, lead and zinc to the bivalent form is incorrect for zinc, which usually reduces it to metal. The very few slips seen indicate the great care taken with the preparation as a whole. An excellent feature is provided by the lists of questions appended to each chapter. There are good author- and subject-indexes.

At its moderate price the book should prove attractive to students, and, in fact, because of its modern treatment, to all concerned with inorganic analysis.

S. G. CLARKE

LE CONTRÔLE ANALYTIQUE DANS L'INDUSTRIE CHIMIQUE MINÉRALE. A. SANFOURCHE, Ing. Chim., D.ès Sc. Pp. 547. Paris: Masson et Cie. Price 120fr.

This book, written by the head of the central laboratory of the Compagnie de Saint Gobain, concerns itself exclusively with the control and examination of the products of the manufacture of inorganic chemicals. It is not, and does not pretend to be, a text-book of inorganic analysis, neither does it deal with analysis connected with metallurgy, ceramics, etc., but within its limitations it is a valuable laboratory manual. Descriptions of processes have a Gallic clarity which is not always to be found in text-books, and within its covers is a very large amount of analytical wisdom; whether this wisdom, once lost sight of, will readily be refound, is perhaps not quite so certain, as the index is not all that one might wish, and cross-references apparently do not exist.

The book is divided into four sections—"Generalities" (64 pp.), "Heavy Chemical Industry" (154 pp.), "Fertilizers" (109 pp.), and "Light Chemical Industry" (186 pp.); of these, the last gives the impression of being very much the weakest. While the great bulk of the methods are undoubtedly sound, and while the descriptions leave nothing to be desired, and the comments are admirable, one may perhaps be permitted occasionally to differ from the author as to the wisdom of certain procedures. The titration of thiosulphate with iodine on the assumption that tetrathionate is the product (p. 436) seems to be at least of doubtful validity, and boiling off bromine from a hydrochloric acid solution of mercury (p. 527) would appear likely to result in some loss of mercury. The statement (p. 495) that one may reduce ferricyanide to ferrocyanide with ferrous sulphate is incomprehensible as it stands, and to say that "the separation of bromine from chlorine . . . has only received partial solution" (p. 358) argues a lack of acquaintance with the fairly large amount of work done in other countries. Apart, however, from these few criticisms, and taking the book for what it is intended to be—a guide to the examination of certain definite products—it is a manual of great value, and authoritative in that it seems to embody the established practice of the laboratory of a large chemical firm. Its great weakness, and one which cannot be guarded against, will probably be the change in stress on different impurities which is bound to occur with changing methods of manufacture.

The book is well bound, and the tables of factors with which it abounds should lead to considerable saving of time for those who use it. Proof reading appears to have been careful, though two or three slips are to be noticed. To English eyes the print seems rather pale and the paper rather transparent, but in neither respect unpleasantly so. It is the book of a man who is a master of his subject and who is not afraid to criticise official methods. B. S. EVANS

HANDBOOK OF CHEMISTRY AND PHYSICS. A READY-REFERENCE BOOK OF CHEMICAL AND PHYSICAL DATA. Edited by C. D. HODGMAN, M.S. Twenty-first Edition, 1936–7. Pp. xviii + 2020. Published by The Chemical Rubber Publishing Co., Cleveland, Ohio, U.S.A. Price 25s.

Only last year the twentieth edition of this useful little volume was noticed in THE ANALYST, and now the work may be said to have attained its "majority." It is substantially a book of tables—chemical, physical and mathematical, textual matter occupying less than one-tenth of the total space and consisting largely of definitions and brief explanations of fundamentals. The analyst will not go to it for descriptions of methods, but it is the kind of book to have always at hand in the laboratory or at the desk. The present edition contains 70 pages more than its predecessor. The new matter includes, besides some physical and mathematical data, a 17-page table of the properties of some commercial plastics, an extension of the section on Laboratory Arts and Recipes from 8 to 17 pages, a considerable extension of the photographic section, a list of isotopes (which now occupies 6 pages instead of 3), and one addition to the tables of densities of aqueous solutions—that of perchloric acid. No change appears to have been made since the last edition in the main tables of the physical properties of chemical compounds (about 400 pages).

The qualities of most importance in a book of this kind are reliability and handiness. The accuracy of the older matter may reasonably be taken for granted in a twenty-first edition, and if the absence of misprints and other patent errors is indicative of the care given to the selection of the newer matter, this also may be accepted with confidence. The reviewer has encountered no mistakes in the course of some months' use of the book. As to its handiness, its page size is small (4 by 6½ ins.), and, notwithstanding the use of thin paper, its 2000 pages make it a rather stubby volume. Its limp cover and fine finish, however, render it very convenient to handle, and it will lie open at any page without any strain on the binding, but there is at times some inconvenience in reading to the middle of a double page. In a book to be read continuously this would become intolerable, but in a reference book it seems to the reviewer a minor inconvenience compared with that of having two volumes and finding that the wrong one usually comes to hand first, or that the index has to be consulted in one volume and the required matter in the other.

J. H. LANE

BOOKS AND DOCUMENTS. By J. S. GRANT, Ph.D., F.I.C. Pp. xii + 218, with 36 illustrations, including 12 plates. London: Grafton & Co. 1937. Price 10s. 6d.

This volume is intended for the use of all who are engaged in any way in the manufacture, use and investigation of paper, inks and books, and although many readers may not find the whole text of interest, much will prove useful to the majority, and the author has met with considerable success in an ambitious attempt.

The subject-matter is divided into two parts, the first dealing with the dating of books and documents and including the history of paper-making, dating from the evidence provided by the paper, ink and other materials, chemical and physical tests (the latter illustrating the great value of filtered ultra-violet radiation for differentiation), and the detection of erasures, faded writing and ordinarily invisible inks. Part II contains a wealth of information on the permanence and preservation of books and documents from all points of view, tests for stability, the effects of light, heat, air and moisture, the selection of, and specifications for, papers and inks, and future methods for the production of permanent records. The volume is completed by a combined name and subject index which is both comprehensive and accurate.

Throughout the text there is evidence of the author's industry and care in compilation, and the abundant cross-references should ensure that the reader misses nothing relevant to the subject. In addition, a bibliography at the end of each chapter provides a guide to other books and scientific papers in which more detailed information may be found.

The illustrations in the text and the plates are good, with perhaps the exception of Fig. 36, but there is no obvious reason why a dissecting lens, two needles and a bottle should be displayed on a plate instead of as text figures. Since the illustrations are not arranged in strictly numerical order, reference to them would be facilitated by quoting the page in addition to the figure number of each.

On p. 45 the statement is made that "the various dating tests . . . can be used by workers having little or no knowledge of the methods of experimental chemistry or physics," and whilst this is certainly true, it would be a highly dangerous procedure to allow so ill-equipped a worker to operate on a document valuable on account of its age, rarity, or the likelihood of its becoming a court exhibit, for irremediable damage may easily be done. It is to be regretted that some of the chemical tests described do not justify the confidence which is often placed in their results. Thus a blue colour on the addition of iodine solution, as described on p. 61, does not necessarily indicate the presence of starch, for the same reaction is given by some hydro-, oxy- and nitro-celluloses, saponins and other compounds liable to occur in or on paper. The Herzberg chlor-zinc iodine test described on p. 48 is widely used, but at the best gives uncertain results, and the reviewer has been greatly puzzled at times when, on applying the test, some fibres are coloured blue at one end and brown at the other. Many varieties of stylographic pens do not yield the type of stroke described on p. 40, for not infrequently one finds the track of the central wire as a darker line within the stroke, and some writers when using these pens habitually produce strokes of uneven thickness, especially when certain inks are used.

The proof reading has been carefully done, although a few minor errors have escaped correction. Thus on p. 65 Prussian blue is stated to yield a *blue* ash on ignition; "methylacetate" on p. 194 should evidently be preceded by the word "cellulose"; on p. 27 the spelling of "encyclopaedias" is rather mixed, whilst a little ambiguity about the storage of loose sheets occurs on p. 175, where presumably "flat" should be interpreted as "horizontally."

Within the limits of a comparatively small volume the author has included an abundance of diverse information and has produced a work which will merit a wide appeal. It will prove of distinct service to all interested in the preservation of books and documents—a subject of outstanding importance in the recording of a nation's activities.

T. J. WARD

AN INTRODUCTION TO ORGANIC CHEMISTRY. By ALEXANDER LOWY, Ph.D., and BENJAMIN HARROW, Ph.D. Pp. xiv + 429. Fourth Edition. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1936. Price 15s. net.

Introductions to organic chemistry are so numerous and, for the most part, so much alike that the mere sight of one is apt to cause a feeling of ennui. With Lowy and Harrow's book, however, this feeling, if it arises at all, is rapidly overwhelmed by one of eager interest which is maintained until the end, for although the traditional divisions of the subject (aliphatic, aromatic, heterocyclic, etc.) are adhered to, there are many features which do not commonly occur in text-books.

At the very beginning of the book the student, if he reads the introductory chapter, is made to realise that organic chemistry is not a useless subject, but one that enters into every phase of living activity, and throughout the text the authors lay stress on its connection with medicine, dentistry, agriculture, and industry—in short, the uses of compounds rather than their physical constants are recorded. In the body of the book are numerous charts summarising the manufacture, the derivatives or uses of the more important compounds. The human interest is also brought in by the inclusion, in appropriate places, of photographs of great organic chemists. To each photograph is attached a suitable biographical note. The inclusion of chapters on such subjects as "Foodstuffs and their Changes in the Body," "Dyes and Stains," and so on, also add to the interest of the book. The work ends with a chapter on nomenclature, an extensive list of special books, a glossary of unusual words (mostly medical) and an index.

The authors have included chapters on such advanced subjects as Enzymes, Vitamins and Hormones, Plant and Animal Pigments, and Vegetable Alkaloids. Even Schoenheimer's work on the use of heavy hydrogen in tracing the course of fat metabolism receives mention. In an elementary book such subjects must of necessity be inadequately treated (the alkaloids are dismissed in 3 pages), and although they are of great importance and absorbing interest, their inclusion tends to bewilder the elementary student.

American spelling, of course, is to be expected, but few British chemists will readily tolerate the terms mono, di and tri *atomic* alcohols.

Although readers with a deep knowledge of organic chemistry and very critical minds might be inclined to regard this book as superficial in some respects, yet it is well written and excellently produced. It presents the beginnings of organic chemistry in an unusually interesting way and cannot fail to arouse in the student a desire for more. HAROLD TOMS

STEDMAN'S MEDICAL DICTIONARY. Thirteenth Edition. By T. L. STEDMAN, A.M., M.D. Pp. xii + 1291. London: Baillière, Tindall & Cox. 1937. Price 35s.

Medicine is steadily tending to become a branch of applied biochemistry, and pathological conditions are now studied as manifestations of the sum of chemical reactions that have followed an abnormal course and require chemical control. A striking proof of this dependence of medicine upon chemistry is afforded by a comparison of this new edition of *Stedman's Medical Dictionary* with various standard medical dictionaries. In the present work drugs are defined in chemical terms, and chemical tests (*e.g.* the Reinsch test) are not merely mentioned, but also described in brief outline.

This exceptionally full treatment of the chemical side of medicine does not, however, involve neglect of the medical side, for the ground is thoroughly covered; one will find here fully explained both the common and the less known terms used in anatomy, pathology, medicine, surgery and pharmacology. There is also a useful introductory section on medical etymology and the correct method of word-building in medical science.

Bacteriology is fully dealt with, and there is an appendix of 15 pages, giving the morphology, cultural and staining properties, and pathogenicity of the principal pathogenic micro-organisms. Another appendix contains an alphabetical table of drugs, with their doses and therapeutic indications; this is based on the U.S. Pharmacopoeia XIth Revision, and the National Formulary, 6th Edition.

As the work is of American origin, transatlantic spelling has been adopted for certain words, such as "sulfur," for which, until recent years, American doctors used the English form, "sulphur."

To sum up, this dictionary will be found invaluable by biochemists who wish to follow the significance of technical papers in the medical press, and by medical men and veterinary surgeons who are alive to the chemical development of their subjects and wish to understand the meaning of chemical terms that are now in daily use. EDITOR

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Death

WITH great regret we record the death, on September 7th, of Joseph Harold Totton.

"Resins" and "Pitch" from Ancient Egyptian Tombs

BY J. G. A. GRIFFITHS, B.A., PH.D., A.I.C.

(*Read at the Meeting, May* 5, 1937)

THE opportunity of attempting to establish the nature and, if possible, the identity of four dark, somewhat pitchlike, substances found in Egyptian tombs was afforded by Mr. A. Lucas, who kindly supplied the specimens.

In carrying out the investigation it was constantly borne in mind that, in general, naturally occurring resinous materials are complex mixtures of organic substances of uncertain constitution, prone to undergo oxidative and other changes during storage. Thus, as a result of keeping, the "saponification value" of colophony and the proportion insoluble in light petroleum are increased and the acid value is decreased. Furthermore, changes that are scarcely perceptible during a few years may have, over a period of three thousand years, such a cumulative effect as to alter in a marked manner the chemical and physical properties of a "resinous" substance. Caution is therefore necessary in using analytical data to classify such a material by comparison with the data derived from authentic specimens of recent origin.

It might be expected that part of the more volatile of the odoriferous ingredients of the specimens would be lost during the course of three thousand years, and further, that the substances giving the characteristic odour might have undergone oxidative or other changes. For these reasons the odour of the sample, or of the fractions derived from it, cannot be regarded as a certain guide to identity.

Concerning these points, it is of interest to note that the material extracted by light petroleum from the above Egyptian specimens became partly insoluble in that solvent after being kept for some months. Also, the original specimens gave positive "abietic acid" reactions (pp. 705, 706), but after being kept for some months in a powdered condition, gave negative results. These observations show that changes which may have been proceeding slowly for three thousand years are not yet complete in the lumps of "resin," but occur relatively rapidly during suitable exposure to the atmosphere. It is clear that at least partial solubility in light petroleum and a positive "abietic acid" reaction were properties of the specimens about three thousand years ago.

Lucas[1] has suggested the following criteria whereby resins, gums, bitumen and mineral pitch, and wood pitch, found in ancient remains, may be distinguished:

(1) Resins are freely soluble in ethyl alcohol, and either insoluble, or only slightly soluble, in water.
(2) Gums are freely soluble in water, and either insoluble, or only slightly soluble, in alcohol.
(3) Bitumen and mineral pitch have low solubility in alcohol, a high content of sulphur, and a comparatively high solubility in light petroleum.
(4) Wood pitch has a high solubility in alcohol and a comparatively high solubility in light petroleum.

Further, under the influence of ultra-violet light in the range 300–400$m\mu$, resins are stated to give a strong fluorescence varying in colour from yellow to brown, whilst it is only in certain solvents that bitumen fluoresces.

More recently, Spielmann[2] has shown spectrographically that the ash of natural bitumens contains vanadium, nickel and molybdenum, whilst resins contain only the smallest traces, or none, of these metals.

In the present investigation the analysis was directed towards obtaining such particulars as would enable deductions to be made in the light of the foregoing considerations. In addition, certain colour tests were found to have diagnostic value.

The examination of the samples is divided into two parts—a quantitative analysis and a qualitative investigation.

EXAMINATION OF THE SAMPLES.—The samples examined were labelled as follows:—(1) "From Jar XIXth Dynasty, 1875/20" (Tomb of Menephtah)**; (2) "Canopic Coffin No. 1, Tut-ankhamun"††; (3) "Canopic Jar, 'Queen Tye,' 94/31"; (4) " ? Wood Pitch, from mummy, 7/33." All the samples were black lumps.

Quantitative Analysis.—The fractions soluble in light petroleum (b.p. 40°–60° C.) followed by ether, and, with a fresh portion of the powdered sample, the fractions soluble in cold and hot absolute alcohol, followed by hot water, were determined.

Any fat, and certain fractions of the resins or pitch, dissolved in the light petroleum, and further examination of the solute decided whether fat was present. The alcohol-soluble matter was regarded as a measure of the resin present, whilst the amount of water-soluble material gave some idea of the proportion of gum, due regard being paid to any water-soluble mineral or other matter.

** *Cf.* A. Lucas, ***Ancient Egyptian Materials and Industries***, p. 257.

†† *Cf.* Lucas, *op. cit.*, p. 256–7.

Acid and saponification values were also determined, and the proportion of sulphur was found by Eschka's method. The results are shown in Table I.

TABLE I

QUANTITATIVE DATA

	Sample No.	1.	2.	3.	4.
I.	Specific gravity..	1·14	1·21	1·09	1·13
II.	Volatile at 100° C., per cent.	4·0	4·6	7·5	21·2
III.	Soluble in light petroleum (b.p. 40°–60° C.), per cent.	19·5*	2·2†	39·9‡	24·5‡
IV.	Soluble in ether (includes III), per cent. ..	63·7	21·2	63·0	47·1
V.	Soluble in hot absol. alcohol, per cent. ..	89·7	43·5	68·5	50·4
VI.	Soluble in cold absol. alcohol, per cent. ..	81·6	40·3	66·1	49·7
VII.	Water-soluble of hot-alcohol-insoluble, per cent.	0·4	18·8§	1·0	0·5
VIII.	Water-soluble of ether-insoluble, per cent. ..	—	26·2‖	—	—
IX.	Water-insoluble of hot-alcohol-insoluble, per cent.	6·0	32·4	23·8	27·4
X.	Sulphur, per cent.	0·67	2·20	1·84	0·02
XI.	Ash, per cent.	0·17	12·8¶	1·9	1·1
XII.	Phosphoric oxide (P_2O_5), per cent.	—	0·13	—	—
XIII.	Acid value (duplicate determinations) ..	101 94	90 101	34	24
XIV.	Saponification value (duplicate determinations)	175 163	197 199	64	54
Total of II, V, VII, IX	.. ..	100·1	99·3	100·8	99·5

The several fractions had odours consistent with a coniferous origin; they were dried at 100° C. to constant weight.

The proportions of all fractions are calculated as percentages of the original substance.

* Included approximately 10 per cent. of fatty acids.

† Probably partly fatty acids.

‡ Fatty acids were not found in these fractions.

§ Contained 7·3 per cent. of ash consisting almost entirely of Na_2CO_3 (4·6 per cent.), Na_2SO_4 and NaCl.

‖ The aqueous solution was dark brown and contained 9·0 per cent. of ash consisting of water-insoluble (0·8 per cent.), Na_2CO_3 (1·2 per cent.), Na_2SO_4 (6·0 per cent.), and NaCl (1·0 per cent.).

¶ Contained water-insoluble (2·7 per cent.), Na_2CO_3 (0·2 per cent.), Na_2SO_4 (8·1 per cent.), and NaCl (1·6 per cent.).

Qualitative Examination.—(1) The *Liebermann-Storch* reaction was carried out on the fractions extracted with sodium hydroxide solution from the ether-soluble and the light petroleum soluble portions of the substance. Like colophony, *Cedrus libani* resin, after being melted, gives a strong purple colour. Wood (Stockholm) tar gives a purple colour which changes very rapidly to brown.

(2) The *Halphen-Hicks* reaction did not give any guidance.

(3) The "*abietic acid*" test:—The light petroleum extract of the "resin" was washed several times with water and then shaken with an aqueous solution of copper acetate. The copper salts of abietic and related acids are soluble in light petroleum, giving blue-green solutions. It was found that the colour produced by the resin of *Cedrus libani*, sandarac, mastic and olibanum was generally of a bluer hue than that due to colophony. Elemi, copal and dammar gave only very faint positive reactions, whilst ammoniacum and myrrh gave negative results. Wood (Stockholm) tar gave a strong positive reaction.

(4) The test for *wood pitch*[8] was applied to the sodium hydroxide extract of the dried acetone extract of the "resin." Diazobenzene chloride gives a red colour in the presence of wood pitch. Colophony gives a yellow colour in this test.

(5) Tests for *phenols*. The aqueous extract of the fraction soluble in ether and sodium hydroxide was treated with

(*a*) very dilute ferric chloride.

(*b*) sodium hydroxide and diazotised sulphanilic acid.

(6) Test for *nitrogenous substances*. The specimen was heated with lime, and ammoniacal products were sought for in the gases evolved.

(7) *Microscopical Examination*.—The original material was extracted, as far as possible, by a series of solvents, and the insoluble residue was treated with chloral hydrate and examined for characteristic tissues, etc.

(8) The *spectroscopic examination* of each ash was kindly carried out by Dr. A. E. Martin of the Government Laboratory.

TABLE II

QUALITATIVE EXAMINATION

Sample No.	1.	2.	3.	4.
Fracture	Resinous, friable	Irregular, friable	Conchoidal, bright	Conchoidal, bright
Colour of powder	Burnt sienna	Chocolate	Black	Dark chocolate
Fusibility	Semi-molten at 100° C.	Melts above 100° C.	Very viscous liquid at 100° C.	Sinters at 100° C.
Fluorescence in ultra-violet light (300–400$m\mu$)	Very strong burnt sienna similar to aloes	Faint velvety brown	Velvety brown	Faint velvety brown
Spectroscopic analysis of ash (Mo, Ni, V)	Mo, Ni, V	Mo, V	Mo, Ni, V	V
Liebermann–Storch reaction	Red-brown	Pink, changing to brown	Slight darkening	Faint red-brown
"Abietic acid" test	Strong green	Strong green	Green colour	Pale green
Test for wood pitch (Lunge and Keane)	Yellow	Yellow	Yellow, changing to orange	Orange-red
Tests for phenols (ether-NaOH soluble):—				
Aq. solution + $FeCl_3$	Yellow	Yellow	Pale yellow	Pink-yellow
Aq. soln. + NaOH + diazotised sulphanilic acid	Pale yellow	Yellow	Pale yellow	Orange
Test for nitrogenous substances	Negative	Strong positive	Weak positive	Weak positive
Microscopical examination	Tracheids (some with pitted walls) A few fibres similar to cotton	Tracheids with bordered pits characteristic of coniferae Numerous fibres, possibly linen	Traces of unidentifiable vegetable matter	Traces of unidentifiable vegetable matter

Although authentic specimens of numerous resins were available for examination (in several instances through the kindness of Mr. T. E. Wallis, of the Pharmaceutical Society), it was not possible to examine, for the purposes of comparison, genuine juniper resin or pitch. Thus, it was not possible to test whether any of the four substances was a juniper product, as seemed likely from the views expressed by Lucas[4] about similar substances.

CONCLUSIONS.—*Sample* 1.—The data indicate that the substance is probably a resin mixed with about 10 per cent. of fatty matter. The strong green colour acquired by the light petroleum layer in the "abietic acid" test indicates that the resin may have come from a coniferous tree, but the colour produced by the Liebermann-Storch reaction shows that it is probably not of the nature of a pine or cedar resin. It may have been sandarac.

Although the ash contains traces of molybdenum, nickel and vanadium, the low proportion of sulphur would seem to exclude the presence of mineral bitumen, particularly as Spielmann[2] has found traces of these tell-tale metals in resin.

Sample 2.—The high content of sodium salts corresponds with the presence of about 9 per cent. of natron, but the composition of the original natron cannot be deduced, owing to reactions between the natron and the material with which it was mixed. Vegetable debris, partly of coniferous origin, is also present. There is probably some animal matter, indicated by the phosphorus-content, traces of fatty material, and evolution of ammonia when the specimen was shaken with lime. After allowance is made for the effect of these constituents on the analytical data, it seems that the other ingredient, amounting to about half of the total, is probably a resin. Mineral bitumen is absent. The resin may be of coniferous origin, but the colour produced by the Liebermann-Storch reagent seems to rule out the possibility of pine or cedar resin.

Sample 3.—The data for this substance are consistent with wood pitch. The sample may, however, contain mineral bitumen, as suggested by the presence of traces of molybdenum, nickel and vanadium; but the proportion must be small, since the percentage of sulphur is low. It appears that the substance consists of wood pitch, possibly of coniferous origin but probably not derived from pine or cedar, with possibly a small addition of mineral bitumen.

Sample 4.—The data for this substance are consistent with those of a wood pitch of coniferous origin. Mineral bitumen is absent. This ancient wood pitch is particularly interesting for the retention of its high proportion of matter volatile at 100° C.

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DISCUSSION

Dr. H. E. Cox congratulated Dr. Griffiths on the very interesting data which he had presented and his courage in bringing forward his conclusions. He, himself, had had an opportunity a few years ago of examining about 20 specimens of similar material and he well remembered attacking the problem with hopefulness, but as time went on hopefulness evaporated and in the end he came to the conclusion that, while it was not difficult to determine a number of chemical facts and figures, it was very difficult indeed to draw any valid conclusions from the results obtained.

Whatever figure or reaction was considered, it was impossible to forecast with any certainty what would be the effect of time when years were measured by the thousand, and it was very noticeable from the literature that different people working on the same material interpreted their figures in quite opposite ways. He noticed that the figures obtained for the specific gravities were very high. Such figures were given by myrrh and galbanum. In the case of sample No. 1 the high proportion of fat might reduce the specific gravity; on the other hand, it might be urged that the more volatile parts of myrrh would evaporate in 3,000 years, and in the matter of data based upon solubility, there was evidence that resins originally soluble tended to become less soluble or insoluble on long exposure to air. He thought that records of figures were of much value and that at some more distant time it might be possible to interpret the accumulated data with more confidence.

Mr. R. L. COLLETT said that some fifteen years ago he was given some portions of a chair from Tut-ankhamun's tomb by Mr. Lucas, who believed that it might be leather. Microscopic examination of these pieces showed that they were leather —and moreover goat skin. However, on making determinations on the small quantities that were available, he was surprised to find that there was no nitrogen present, and he therefore thought that the fragments seemed, chemically, to be of a resinous nature.

Mr. C. L. CLAREMONT asked whether all the specimens had come from the same tomb; if so, one would expect them to give the same analytical results.

Mr. A. L. BACHARACH called attention to the difficulty of using diagnostically differential solubilities in several solvents of the various substances in complex mixtures; it was well known that the solubility of a substance was strongly influenced by the presence of some other solute, especially when both were of a complex nature. Hence it would be important, if differential solubilities were used for analytical purposes, to devise strictly reproducible methods, and he doubted if a single continuous extraction could be so described.

Dr. B. S. EVANS asked whether the presence of traces of molybdenum, nickel and vanadium was always indicative of Judaean bitumen, or was it a characteristic of bitumen in general.

Mr. L. EYNON asked if the four samples were of the same or different periods.

Dr. GRIFFITHS, replying to Dr. Cox, said that he accepted the authority of Dieterich that the specific gravity was not of very great diagnostic value. He (Dr. Griffiths) had suggested, for example, that the material of sp. gr. 1·14 (sample 1) was substantially a resin of the nature of sandarac. The value given in the present paper did not greatly exceed the observed specific gravity of some samples of sandarac, and an increase of specific gravity might well result from loss of volatile matter (as mentioned by Dr. Cox), polymerisation or oxidative changes occurring during 3,000 years. Some copals were reported to have high specific gravity. Respecting the unknown changes which substances might possibly have undergone during 3,000 years he (Dr. Griffiths) had found that the light-petroleum-soluble fractions of the Egyptian specimens he had examined became partly insoluble in that solvent after being kept for some months, and modern colophony underwent a somewhat similar change on keeping. With the exception of sample 2, it appeared probable that the specimens had not changed very greatly with age.

The change mentioned by Mr. Collett was interesting, as Lucas had reported on the examination of pieces of mummy tissue, and the solubility figures obtained suggested that the materials were of the nature of resin.

In answer to Mr. Claremont, the specimens were not taken from the same tomb. Different "resinous" substances had been found in the same tomb, but if there were evidence of a "resinous" fluid having been poured, for example, over the contents of four canopic jars in succession, then, assuming the homogeneity of the fluid, one would expect the analyses of the "resinous" substances from the jars to agree, provided that the different visceral material in the four jars had had similar action, if any, on the four portions of resin.

Replying to Mr. Bacharach and Mr. Evers, the author considered that, although the analytical figures obtained by applying solvent extraction processes to "resinous" substances might not be exactly reproducible, nevertheless, the figures obtained had a very definite value in giving the relative magnitudes of the solubilities in the different solvents. He regarded the extraction with solvents as a sorting test.

Replying to Dr. Evans as to the diagnostic value of traces of the three elements, molybdenum, nickel and vanadium, Dr Griffiths understood that traces of these three elements were always present in mineral bitumen (*cf.* Spielmann, *J. Egypt. Arch.*, 1932, **18**, 177; Goldschmidt, *J. Chem. Soc.*, 1937, 668); they also occurred in some resins. If traces of these three elements were not present in a material, it meant that mineral bitumen was also absent; in other words it was an exclusion test.

In reply to Mr. Eynon, Dr. Griffiths said each sample was taken from a different tomb, and all were of about the same period.

A New Apparatus for the rapid and economical Determination of the Freezing-point of Milk

By PETER L. TEMPLE

(*Read at the Meeting, May* 5, 1937)

For the routine determination of the freezing-point of milk the form of apparatus described by Hortvet in 1921[1] has long been accepted as the most suitable cryoscope. A cryoscope of this design has been in use at the National Institute for Research in Dairying for over eleven years and has given uniformly satisfactory results. The apparatus possesses, however, a certain number of disadvantages. Captain J. Golding therefore suggested that I should investigate the possibility of improving the technique of using it, while retaining the satisfactory principles involved. He also suggested that, in view of the fact that a method for the determination of the freezing-point of milk is under consideration, it is desirable to explore the potentialities of certain modifications in design.

The most serious disadvantages of the Hortvet apparatus are the following:—(1) The manual control of the cooling medium; (2) the considerable expenditure of time and material requisite to carry out each determination; (3) the use of ether and the consequent need to dispose of a disagreeable and potentially dangerous vapour; (4) the fact that the apparatus is designed for a permanent home in a laboratory rather than for general use in the industry.

In the apparatus described in this paper the temperature-control of the cooling medium is entirely automatic. It is easily possible to carry out twelve determinations per hour without previous cooling of the samples, while with the Hortvet apparatus one cannot rely on making more than four determinations per hour, even when the milk is already chilled. Ether has been entirely eliminated from the present apparatus and all the cooling materials are circulated in a closed system. This results in a very substantial saving in time and material.

The essential principle of this apparatus is that the measurement takes place in a bath of calcium chloride solution of such a concentration as to freeze at —2·3° C. This temperature is continuously maintained by circulated brine thermostatically controlled at —5° C. The brine is cooled by a Frigidaire SO_2 compressor unit. The general arrangement is shown in Fig. 1.

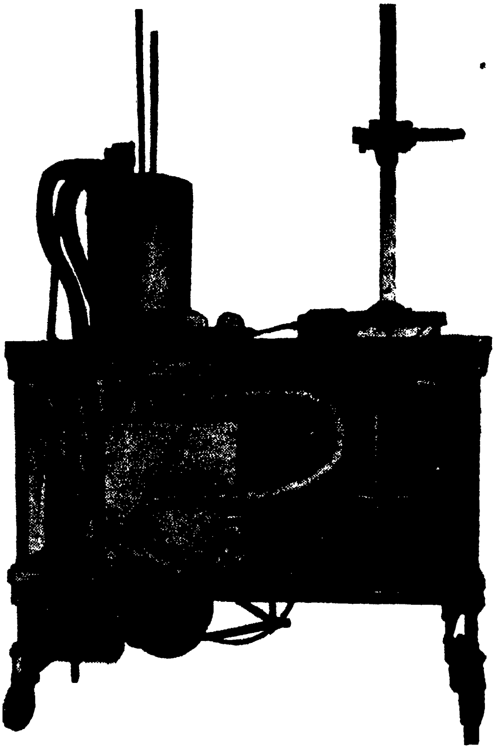

FIG. 1.

The cryoscope chamber (Fig. 2, p. 712) is a brass cylinder, 6 in. in internal diameter and 12 in. in height, closed at the lower end and lagged with 2 inches of cotton silicate. In the top of the cylinder is a brass lid, drilled to take two metal tubes such as are used in the Hortvet apparatus, a ⅜-inch bush to hold the control thermometer and a 1¼-inch bush into which is fitted a gear-box which drives the stirrer. The bulb of the control thermometer is in the centre of the brine, and the two metal tubes and the shaft of the stirrer form a triangle round this. These in turn are surrounded by the cooling coils consisting of four 15 ft. lengths of copper tubing through which brine circulates.

Beneath this chamber is a ½ cb.ft. brine tank containing a 40-ft. expansion coil connected with the Frigidaire SO_2 compressor unit. The tank also contains the bulb of a Bourdon-tube type thermostat which switches the compressor motor at —5° C., with a tolerance of ±0·3° C. The brine is circulated through the cooling coil in the cryoscope chamber by a small centrifugal pump at about

200 gallons per hour. The pump-motor also drives the stirrer by means of a flexible shaft and a gear-box which reduces the speed to 700 r.p.m.

The whole apparatus is mounted in a light steel frame on castors. It can easily be moved from one laboratory to another and only requires to be plugged into the electric supply to be ready for service.

The technique of working is similar to that of the Hortvet with two exceptions: —(1) The stirrer is switched off between the time at which the sample is seeded and that at which the reading is taken; (2) the space between the tube of milk and the surrounding brass tube is filled with alcohol to a level considerably higher than is recommended for the Hortvet.[3] These modifications have not been found to introduce any disadvantages, and the second one probably contributes somewhat to the increased speed of working. The major increase in speed is due to the much higher rate at which it is possible to cool the samples without running the risk of error associated with very low bath-temperatures. This is due to the vigorous stirring, to the high specific heat and thermal conductivity of calcium chloride solution (relative to ether), to the higher level at which the solution stands round the brass tube and to the fact that the temperature of the bath is buffered at −2·3° C. by the latent heat of freezing of the solution. Owing to this buffer-action and the consequent strict and automatic temperature control there is less danger of error from excessive super-cooling than with the older type of apparatus.

TABLE I

	New apparatus			Hortvet apparatus		
	Average freezing-pt.	Number of determinations	Range ±	Average freezing-pt.	Number of determinations	Range ±
15th Feb. 1937	−0·541	4	0·0015	−0·542	4	0·002
16th ,, ,,	−0·543	3	0·0015	−0·542	3	0·0025
17th ,, ,,	−0·543	3	0·001	−0·543	3	0·001
18th ,, ,,	−0·538	3	0·0015	−0·539	3	0·003
19th ,, ,,	−0·546	3	0·001	−0·544	3	0·002
22nd ,, ,,	−0·543	3	0·001	−0·546	3	0·001
23rd ,, ,,	−0·549	3	0·001	−0·550	2	0·0005
17th Mar. ,,	−0·543	3	0·0005	−0·543	2	0·0015
1st Apr. ,,	−0·545	4	0·001	−0·545	3	0·002
2nd ,, ,,	−0·542	6	0·001	−0·543	2	0·0015
5th ,, ,,	−0·542	5	0·001	−0·540	2	0·003
6th ,, ,,	−0·543	5	0·001	−0·543	2	0·001
7th ,, ,,	−0·540	4	0·001	−0·540	2	0·0015
8th ,, ,,	−0·539	3	0·0005	−0·538	2	0·0005

	New apparatus	Hortvet apparatus
Standard error of a single reading—		
(1) on water	0·00110	0·00112
(2) on milk	0·00104	0·00183
Probable error of single determination ..	0·00105	0·00145

In Table I typical results obtained with this apparatus are compared with the values given by the Hortvet apparatus for the same series of samples. In 13 out of 14 cases the difference between the average values given by the two methods lies within the range given by the Hortvet apparatus. The fact that the difference is positive in 6 cases, negative in 6 cases and zero in 2 cases, indicates that there is no systematic difference between the two methods. The mutual consistency of the separate measurements on one sample is better with the present apparatus than with the Hortvet apparatus in 9 determinations. In only one instance is it not as good. The relative consistency of the two methods is more accurately estimated by comparing the standard deviation of readings and probable errors of single determinations, as given at the foot of Table I. It will be seen that the probable error of the present apparatus is just less than three quarters of that of the Hortvet apparatus. All readings were taken with the aid of a cathetometer.

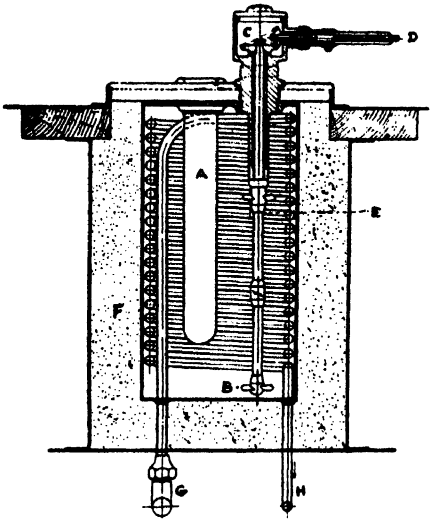

FIG. 2.

(A) Freezing-tube; (B) Stirrers; (C) Gear box; (D) Flexible shaft; (E) Brine coil; (F) Lagging; (G) From pump; (H) To brine tank.

Excluding the first cost and the cost of labour, the only expense of the present apparatus is for power. Taking as a basis of comparison the cost of making twelve determinations, and assuming the price of power to be 1d. per K.W.H., of water 2s. 6d. per 1000 galls. and of commercial ether 2s. 6d. per litre, the Hortvet apparatus involves a cost of 1s. 0½d., and requires at least three hours for twelve determinations. The new apparatus enables the same number of determinations to be made in one hour, at a working cost of only 0·2 of a penny.

I should like to acknowledge my indebtedness to Captain J. Golding for his interest in this work and for many valuable suggestions, to Dr. Paul White for advice on statistical treatment of data, to Frigidaire, Ltd., for very kindly presenting the SO_2 compressor unit and for preparing the drawings from which the illustrations have been made, to the Pulsometer Co., Ltd., for the loan of a vacuum pump used in preliminary experiments, and to Girdlestone & Co., Ltd., for the loan of the centrifugal pump.

Frigidaire, Ltd., are in course of producing a simpler form of cryoscope embodying the principles described in this paper. In their opinion it is possible to do away with the pump and brine tank, further decreasing the size and weight of the apparatus with a smaller motor. They also suggest a smaller compressor using "Freon" instead of sulphur dioxide. As this model is still under construction, it has not been possible to give any data as to its performance.

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The Determination of Mechanical Wood Pulp in Paper

BY S. S. AIYAR, M.Sc., PH.D., F.I.C., AND P. S. KRISHNAN, M.A., A.I.C.

INTRODUCTION.—The Indian Customs Tariff includes a protective duty on (news) printing paper in which mechanical wood pulp forms less than 70 per cent. by weight of the fibre-content. In the Custom House Laboratories in India the official method of determining the mechanical wood pulp is the Spence and Krauss weight-length-factor microscopic method,[1] with the modifications indicated later. The Government Printing Office, United States, has reported that this method gives satisfactory results,[2] and in the Bombay Custom House Laboratory, where about 2000 samples of paper are analysed every year, it has been found to be both rapid and accurate. Occasionally, however, when the verdict goes against an importer, the accuracy of the method is questioned and other methods are suggested. The Norwegian Consul at Bombay invited our opinion on Halse's method,[3] which was claimed by the Norwegian Paper Manufacturers' Association to be the best. This study was therefore undertaken to compare the two methods for accuracy and suitability for routine work.

CUSTOM HOUSE OFFICIAL METHOD.—As already mentioned, the official method is based on Spence and Krauss's work. The pulp and slide are prepared by the well-known procedure described in the literature, but after this stage there are some differences in detail. We employ a magnification of 50 diameters. The eyepiece of the microscope carries a micrometer graduated in millimeter squares, and the side of these small squares is employed as the unit for measuring the lengths of fibres; this is of great help in assessing the proportion of short and broken fibres. The weight factor for sulphite fibre is taken as 0·55 when it is 1·00 for the same length of mechanical wood pulp. These factors are very close to the values obtained by the Forest Products Laboratory, Madison, U.S.A. (private communication). Further, since in our experience most of the (news) printing paper coming into India consists solely of mechanical wood pulp and unbleached sulphite pulp, only Herzberg's stain is used; all the blue (and blue-violet) fibres are taken as sulphite pulp, and by the use of the factors given above the mechanical wood pulp-content is calculated. In practice, duplicate results agree within three units. The microscopic method gives the percentage of mechanical wood pulp calculated on the fibre-content.

HALSE'S METHOD.—Halse uses the modification of Willstätter's method first suggested by Tingle.[4] The amount of lignin in a paper is determined and, by taking certain average values for the lignin-content of mechanical wood and sulphite pulp, the mechanical wood pulp-content of the sample is calculated. The procedure given by Halse is as follows:

One g. of air-dry paper is placed in a wide-mouthed glass-stoppered bottle. Fifty ml. of conc. hydrochloric acid (38 per cent. HCl) are added, and, after the paper has been completely wetted by the acid, 5 ml. of conc. sulphuric acid are carefully added. The bottle is shaken several times during the first few hours, and is allowed to stand overnight at room temperature. The solution is diluted with water, transferred to a 750-ml. beaker, and its volume is made up to about 500 ml. The solution is heated to boiling for a few minutes and allowed to stand until all the lignin has settled. The greater portion of the supernatant liquid is decanted, and the insoluble residue is filtered off on a porous crucible (Alundum R.A. 98), thoroughly washed with hot water, and dried at 100° C. to constant weight.

The proportion of ground wood can be obtained directly from the weight of lignin when the paper does not contain any filler. If a filler is present, most of it will be found in the crucible with the lignin. In that event the residue must be ignited, to burn off the lignin, the filler remaining behind. The weight of "pure" lignin is obtained by difference. From this result the mechanical wood pulp can be calculated by the formula:

$$\text{Mechanical wood pulp, per cent.} = \frac{100(L - C)}{T - C}$$

where L = weight of pure lignin in 1 g. of air-dry paper; T = weight of pure lignin in 1 g. of air-dry ground wood; C = weight of pure lignin in 1 g. of air-dry sulphite pulp.

Halse has recommended the values 0·266 for T and 0·030 for C.

This formula gives the percentage of mechanical wood pulp for the entire paper sample. For the purposes of the Indian Tariff, however, the basis for calculation is the percentage of mechanical wood pulp on the fibre-content. The official microscopic method gives the results on the fibre basis. In order to obtain comparable results by the lignin method on that basis we have had to work on two assumptions, both inherent in Halse's formula. As Halse has given the lignin-contents of only air-dry pulps, we have had to assume the moisture present in air-dry paper samples to be entirely from the fibre. The second assumption is that the whole of the sample, less the ash, is "fibre."

TABLE I

ANALYSES ON ORIGINAL UNTREATED SAMPLES OF PAPER

Serial No. of papers	Moisture Per Cent.	Ash Per Cent.	Pure lignin in 1 g. of sample mg.	Pure lignin in 1 g. of ash-free sample mg.	Mech. wood pulp on the basis of pure lignin in ash-free sample Per Cent.	Mech. wood pulp by official microscopic method Per Cent.
2 ..	9·15	10·1	184	204·6	74·0	70·9
3 ..	8·25	11·95	188	213·5	77·8	75·6
4 ..	9·05	8·4	176	192·1	68·7	74·2
6 ..	9·5	0·3	243	243·7	90·6	89·7
8 ..	8·0	13·45	187	216·1	78·9	76·2
12 ..	7·4	33·4	134	201·2	72·5	59·0
Standard 60 per cent. mech. wood pulp..	8·8	1·2	163	165	57·2	60·7
Standard 50 per cent. mech. wood pulp..	8·6	1·1	129	130·4	42·5	50·3

Note.—In column 6 Halse's lignin values for mechanical and sulphite pulps are used for the calculations.

EXPERIMENTAL.—We have examined a few samples of paper by Halse's method, and the results are summarised in Table I, in which column 6 gives the mechanical wood pulp by the lignin method, and column 7 the mechanical wood pulp by the official microscopic method. It will be noticed that the two results are quite close in some instances, but differ considerably in others.

Halse employs air-dry samples of paper; but the air-dry condition is indefinite, depending on the temperature and humidity of the laboratory and also on the nature of the sizing and loading materials. In order to ascertain whether the elimination of this uncertain factor would make the two methods yield more concordant figures, the results by the lignin method were calculated to the ash-free and moisture-free basis, lignin values of mechanical and sulphite wood pulps on the dry basis being used. For this purpose we determined the lignin-contents of an average sample of five mechanical wood pulps taken from different sources and of an average sample of thirteen different unbleached sulphite pulps, both pulps being dried at 100°–105° C. We found 28·8 per cent. and 4·2 per cent. of "lignin" in ash-free and moisture-free samples of mechanical wood pulp and sulphite pulp, respectively. Table II gives the comparative results obtained by the two methods of calculation; they agree closely. Incidentally, this shows that the values adopted by Halse are fair averages for the respective air-dry pulps. The divergence from the optical method, however, still persists, and the reason for this must lie elsewhere. Most papers carry a certain amount of sizing and loading materials. In Halse's method no allowance is made for them. We have attempted, therefore, to remove the size and to determine the lignin in the de-sized material.

TABLE II

Serial No. of papers	Mech. wood pulp on ash-free air-dry samples (Halse's values for lignin-contents of the pulps used) Per Cent.	Mech. wood pulp on ash- and moisture-free sample (Authors' values for lignin-contents of the pulps used) Per Cent.	Mech. wood pulp by official microscopic method Per Cent.
2 ..	74·0	75·6	70·9
3 ..	77·8	78·7	75·6
4 ..	68·7	69·6	74·2
6 ..	90·6	92·4	89·7
8 ..	78·9	79·7	76·2
12 ..	72·5	74·9	59·0
Standard 60 per cent. mech. wood pulp ..	57·2	56·5	60·7
Standard 50 per cent. mech. wood pulp ..	42·5	41·0	50·3

DE-SIZING.—The samples of paper were cut up into small pieces, about 0·25 to 0·5 sq.cm., and a weighed quantity was subjected successively to the following treatments:

(1) Digested with water (20 ml. per 1 g. of sample) on a boiling water-bath for half-an-hour, the water being afterwards poured off.

(2) Digested again with water, as in (1).

(3) Digested with 1 per cent. w/v hydrochloric acid (10 ml. per 1 g. of paper) for half-an-hour on a boiling water-bath, and thoroughly washed with water.

(4) Boiled with two successive portions of alcohol (20 ml. per 1 g.) for half-an-hour each time.

(5) Drained and dried in a steam-oven. The sample was then kept exposed to the laboratory atmosphere at ordinary temperature overnight to regain normal moisture.

Note.—As mechanical wood pulp lost 1·8 per cent. of woody matter by boiling for 15 minutes with 1 per cent. sodium hydroxide solution, paper samples were not subjected to this treatment.

Fourteen samples of paper, including those referred to in Tables I and II, were taken for this investigation. Two of them were papers of known composition made specially for the Government of India by Messrs. Sindall & Bacon of London. The others were typical of the qualities imported into the country as printing paper. They were all de-sized by the procedure outlined above. In de-sizing, the samples lost from 5 to 18 per cent. of their original weight. In all the determinations the lignin was given a final wash with 50 ml. of hot alcohol to remove resinous and fatty products usually present.[5]

Table III summarises the results of analysis of the de-sized samples, by Halse's lignin method and the Customs official method. (The corresponding numbers in the three tables refer to the same sample). To demonstrate the reproducibility of results by the official method we have inserted a column giving the figures obtained at the Lahore Laboratory.

DISCUSSION.—It will be noticed that the two sets of results by the official method are quite close in every instance, but that there is frequently a considerable difference between the results by the lignin method and those by the official method. Sample 1 (Table III) shows the largest difference. When examined under the microscope it was found to contain very little mechanical wood pulp, but the lignin method showed it to contain about 20 per cent. The paper contained a heavy loading of china clay, which in Halse's method remained with the lignin. When the mixture of clay and lignin was ignited to estimate "pure lignin" by difference, the clay was dehydrated and its water of hydration was shown as lignin; the value for lignin was thus increased. Halse has not made any allowance for this in his formula. Samples 11 and 12 gave similar results. Thus in the presence of heavy loading, such as china clay, Halse's method gives abnormally high results.

The results for Samples 7, 13 and 14 are much lower by Halse's method than by the optical method. Riesenfeld's and Hamburger's paper[6] offers one explanation for this. They have pointed out that the lignin-contents of sulphite pulps from different sources vary widely. They have also shown the inaccuracy of applying any fixed set of lignin values for mechanical and sulphite pulps, irrespective of their origin. In the examples given in this paper this may well be the reason, but another explanation is also possible. Although the samples have been subjected to a fairly prolonged de-sizing treatment, it is quite possible that some of the sizing remains. This would be included in the calculation as "fibre," with the consequence that the proportion of mechanical wood pulp would be shown as less than the true value. Without very elaborate treatment it would not be

TABLE III

ANALYSIS ON DE-SIZED AIR-CONDITIONED SAMPLES OF PAPER

No. and description of paper	Results on de-sized air-dry samples		Wt. of pure lignin		Mechanical wood pulp		Mech. wood pulp by official microscopic method	
	Moisture Per Cent.	Ash Per Cent.	in 1 g. of air-dry ash-free sample mg.	in 1 g. of moisture- and ash-free sample mg.	on air-dry ash-free samples (Halse's lignin values for air-dry mechanical wood and sulphite pulps used) Per Cent.	on moisture- and ash-free samples (Authors' lignin values for moisture- and ash-free pulps used) Per Cent.	Bombay Per Cent.	Lahore Per Cent.
1. Light pink, thick art-coated . .	6·56	30·42	78	86	20·3	18·8	about 1	—
2. Deep pink, thin, partly glazed . .	7·93	11·03	217·2	231	79·3	77·5	70·9	71·6
3. Orange, thick, partly glazed . .	7·15	12·35	218·6	238	79·9	79·6	75·6	74·4
4. Yellow, very thick, partly glazed . .	6·59	8·13	215·3	232	78·5	77·2	74·2	73·0
5. Blue, thin, unglazed	10·07	4·67	210·6	235·5	76·5	78·6	76·3	75·2
6. White, thin, unglazed	9·4	0·22	248·2	274	92·5	94	89·7	88·9
7. White, very thin, unglazed . .	8·995	0·2	171	188	59·8	59·6	67·8	66·2
8. White, thin, partly glazed . .	8·38	14·47	216·1	239·6	78·8	80·1	76·2	76·4
9. White, thick, partly glazed . .	6·25	20·84	225·6	245	82·9	82·4	74·6	75·2
10. Yellow, thick, unglazed	6·9	10·9	208·5	226	75·6	74·8	71·9	72·3
11. White, thick, art-coated . .	4·75	33·8	233·9	252	86·4	85·2	76·4	76·8
12. White, thick, art-coated . .	3·25	32·95	215	226	78·4	74·8	59·0	58·5
13. Standard paper 60 per cent. mech. wood pulp	8·0	0·2	156·4	170	53·6	52·4	60·7	61·4
14. Standard paper 50 per cent. mech. wood pulp	8·15	0·15	130·4	142	42·5	41·3	50·3	51·0

possible to remove all the sizing materials, and even then it would be impossible to remove all fillers. This limitation is inherent in all chemical methods.

It remains, then, to account for the virtually normal values obtained with the other samples. This is apparently due to the various factors, mentioned above, tending to operate in opposite directions and so neutralising each other. Since these factors are so uncertain, one cannot be sure of the reliability of the lignin method for the examination of unknown samples.

CONCLUSION.—Halse's method is not suitable for routine work. Even when the sample is not de-sized, the method takes two days. Apart from this, it is subject to severe limitations. While it may give accurate values with paper stocks, it fails with made-up paper because of the presence of loading and sizing materials, which cannot be completely eliminated. Further, while in the optical method it is possible to detect and make allowance for any other fibres that may be present, in Halse's method this is not possible.

The official microscopic method takes only one-and-a-half-hours, and the interference caused by foreign material is negligible. The results of duplicate tests agree within 3 units at the outside, and, judged by our analyses of standard samples, the results appear to be accurate.

In assessing border-line cases, the Government of India makes an addition of 5 units to the percentage of mechanical wood pulp as found by the official method, to allow for possible errors in manufacture and estimation.[7]

In border-line cases the results of the microscopic method are checked by the phloroglucinol method as improved by Dunnicliff and Suri.[8]

Our thanks are due to Dr. H. B. Dunnicliff, Special Chemical Adviser to the Central Board of Revenue, Government of India, for his helpful criticisms, and to Messrs. H. D. Suri and M. Lal of the Board's Control Laboratory at Lahore for carrying out a set of independent tests by the official method.

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CUSTOM HOUSE LABORATORY
BOMBAY, INDIA

The Electrolytic Analysis of White and Yellow Metal Alloys

By SYDNEY TORRANCE, A.R.C.S., B.Sc., D.I.C.

AN electrolytic method for the analysis of white and yellow metals has been worked out by Lassieur.[1,2] Lindsey and Sand[3,4] modified this method for antimony, copper and tin alloys, using the improved form of the Sand calomel auxiliary electrode and other apparatus. Lassieur has experienced some difficulty in separating lead from tin when the amount of lead present was small. This matter has been investigated and a remedy suggested.

Collin[5] has found that the best method of depositing lead is as the peroxide from a 10 per cent. nitric acid solution at a temperature of 90° to 95° C., and with a current of 6 to 6·5 amps. Under these conditions solutions of lead nitrate containing from about 100 mg. down to 2·5 mg. of lead were electrolysed, with the consequent complete deposition of the lead as lead peroxide in twenty minutes. If 5 ml. of 40 per cent. hydrofluoric acid is added to the lead nitrate and nitric acid solution, prior to electrolysis, a minimum of about 25 mg. lead is necessary in a solution of 150-ml. volume to give an anodic deposit of lead peroxide. At lower concentrations of lead no deposit was obtained. With the further addition of 0·2 to 0·3 g. of tin, to simulate the actual conditions in separations of lead and tin, it was found the minimum of lead necessary to produce a deposit was somewhat increased. The production of a deposit was followed by the quantitative deposition of the lead present. When no deposit was obtained, the addition of a further known quantity of lead, in the form of a standard solution of lead nitrate, to bring the lead concentration above the requisite minimum, was sufficient to bring about the subsequent deposition of all the lead present (including that added) as lead peroxide. The amount of lead present initially was obtained by subtracting the amount of lead added from the total deposited. Results thus obtained are given in Table I.

ANALYSIS OF WHITE METAL ALLOYS (*Antimony, Copper, Lead, and Tin*).—From 0·2 to 0·4 g. of the alloy (as drillings or fine sawings) is weighed into a beaker. It may be found convenient to weigh the sample in one of a pair of balanced copper pans. The alloy is dissolved by warming with a mixture of 10 ml. of hydrochloric acid (sp.gr. 1·16) and 10 ml. of distilled water, 1 g. of ammonium chloride being added to minimise loss of tin as tetrachloride. Complete solution may be hastened by the addition, drop by drop, of a saturated solution of potassium chlorate. When all the alloy is dissolved and excess of chlorine has been boiled off, 5 ml. of hydrochloric acid are added, and the solution is diluted to 150 ml. One g. of hydrazine hydrochloride is added, and the liquid is electrolysed at 70°–75° C. at an auxiliary potential of 0·4 volt, a saturated calomel electrode being used. The platinum gauze electrodes, the auxiliary electrode vessel, and the voltmeter are of the type described by Lindsey and Sand.[3,4] The copper and antimony are deposited together, the usual fluctuations described by Lassieur and by Lindsey and Sand (*loc. cit.*) being observed. After fifteen to twenty minutes the current is reduced to a minimum, the liquid in the tip of the electrode vessel is flushed out into the electrolysis beaker, and the electrolysis is continued for a further five to ten minutes. The copper-antimony deposit is then dried and weighed. The copper is separated from the antimony by dissolving the deposit in a mixture of 5 ml. of nitric acid (sp.gr. 1·42), 5 ml. of 40 per cent. hydrofluoric acid and 10 ml. of water, boiling off oxides of nitrogen, diluting to 150 ml., adding a solution of potassium dichromate, drop by drop, until the liquid is distinctly yellow, and depositing the copper by electrolysing the solution for 20 minutes at room temperature at an auxiliary potential of 0·4 volt. The weight of antimony is obtained by difference.

TABLE I

Lead present initially (as PbO_2)	Lead found (as PbO_2)	Further lead added (as PbO_2)	Total lead found (as PbO_2)	Lead "recovered" (by difference) (as PbO_2)
From nitric acid solution				
g.	g.	g.	g.	g.
0·1108	0·1110	—	—	0·1110
0·1108	0·1107	—	—	0·1107
0·0554	0·0557	—	—	0·0557
0·0111	0·0110	—	—	0·0110
0·0056	0·0056	—	—	0·0056
0·0028	0·0029	—	—	0·0029
From nitric-hydrofluoric acid solution. No tin added				
0·1108	0·1109	—	—	0·1109
0·0554	0·0556	—	—	0·0556
0·0277	0·0277	—	—	0·0277
0·0111	—	0·1108	0·1220	0·0112
0·0111	—	0·1108	0·1218	0·0110
0·0056	—	0·1108	0·1163	0·0055
0·0028	—	0·1108	0·1139	0·0031
From nitric-hydrofluoric acid solution. 0·2 to 0·3 g. of tin added				
0·1108	0·1104	—	—	0·1104
0·0554	0·0555	—	—	0·0555
0·0277	—	0·1108	0·1381	0·0273
0·0111	—	0·1108	0·1218	0·0110
0·0056	—	0·1108	0·1165	0·0057
0·0028	—	0·1108	0·1137	0·0029

One g. of hydrazine hydrochloride is added to the solution from which the copper and antimony have been removed by the electrolysis just described, and the tin and lead are deposited together by electrolysing for 20 minutes at room temperature at an auxiliary potential of 0·7 volt. The deposit is dissolved in a mixture of 15 ml. of nitric acid, 5 ml. of hydrofluoric acid and 15 ml. of water, and oxides of nitrogen are boiled off. With high-lead alloys (above 25 per cent. of lead) the lead is deposited as the peroxide, by electrolysing the solution, after dilution to 150 ml., for 20 minutes, at 90° to 95° C., with a current of 6 to 6·5 amps. Low-lead alloys will give a solution containing insufficient lead for deposition from nitric-hydrofluoric acid solution as lead peroxide. For such alloys 20 ml. of a standard 0·5 per cent. solution of lead (as lead nitrate) are added, the mixture is diluted to 150 ml., and the lead is deposited by electrolysing in the usual manner. The deposit of lead peroxide is weighed, and the weight of lead added (calculated to peroxide) is deducted. The corrected weight of lead peroxide thus obtained is calculated to lead by means of the appropriate factor.[5]* The weight of tin is obtained by difference.

The following results were obtained for high- and low-lead white metal alloys:

TABLE II

(*a*) CARRIAGE AND WAGON WHITE METAL (HIGH LEAD)*

Weight of alloy taken g.	Antimony found Per Cent.	Copper found Per Cent.	Lead found Per Cent.	Tin found Per Cent.
0·2500	12·0	2·7	34·2	51·1
0·2500	11·9	2·7	34·2	51·2
0·2500	11·9	2·7	34·2	51·1
0·3000	11·9	2·7	34·3	51·0

(*b*) LOCOMOTIVE WHITE METAL (LOW LEAD)†

Weight of alloy taken g.	Antimony found Per Cent.	Copper found Per Cent.	Lead found Per Cent.	Tin found Per Cent.
0·2500	9·6	6·0	5·0	79·2
0·2500	9·6	6·0	5·2	79·0
0·2500	9·5	6·0	5·0	79·2
0·2500	9·6	6·0	5·1	79·1

* Composition: (*a*) antimony, 11·9; copper, 2·7; lead, 34·0; tin, 51·4 per cent.
† Composition: (*b*) antimony, 9·6; copper, 6·0; lead, 5·1; tin, 79·3 per cent.

ANALYSIS OF YELLOW METAL ALLOYS (*Copper, Lead, Tin, and Zinc*).—From 0·2 to 0·4 g. of the alloy is dissolved in a mixture of 10 ml. of hydrochloric acid (sp.gr. 1·16), 2 ml. of nitric acid (sp.gr. 1·42), 10 ml. of water and 1 g. of ammonium chloride. Five ml. of hydrochloric acid are added, and the liquid is diluted to 150 ml. One g. of hydrazine hydrochloride is added, and the solution is electrolysed for twenty minutes at 50° C. at an auxiliary voltage of 0·4 volt to a saturated calomel electrode. The initial current is 3 to 4 amps., but falls rapidly to about 0·1 amp. All the copper is thus deposited, together with any arsenic that may be present. The copper is freed from the arsenic by dissolving the deposit in a mixture of 5 ml. of sulphuric acid (sp.gr. 1·82), 5 ml. of nitric acid and 10 ml. of water. Oxides of nitrogen are boiled off, and the solution is diluted to 150 ml. and electrolysed for twenty minutes at room temperature, at an auxiliary voltage of 0·4 volt. Copper alone is deposited.

The tin and lead are deposited from the original residual solution and separated from each other as described above.

The solution left after the removal of the tin and lead is oxidised by boiling it with a little bromine until colourless. Ammonia is carefully added until the solution is just alkaline to phenolphthalein, the liquid is heated to boiling, and traces of ferric hydroxide are filtered off. The iron may be determined colorimetrically with thiocyanate[6] after solution of the precipitate in hydrochloric acid. Ten ml. of conc. ammonia (sp.gr. 0·880) are added to the filtrate, which is cooled and electrolysed for twenty minutes at room temperature with a current of 3 amps. The zinc is deposited.

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* The theoretical factor for converting PbO_2 into Pb does not hold for electrical deposits, as there is always a small amount of water absorbed on to the peroxide deposit. Miss Collin (*loc. cit.*) worked out different factors for different weights of deposit; in most instances it was 0·866.

The following results (Table III) were obtained with three bronzes:

TABLE III

(1) Composition:—Copper, 84·6; lead, 3·8; tin, 6·9; zinc, 4·4 per cent.

Weight of alloy taken g.	Copper found Per Cent.	Lead found Per Cent.	Tin found Per Cent.	Zinc found Per Cent.
0·2500	84·4	3·8	7·0	4·5
0·2500	84·5	3·8	7·0	4·4
0·2500	84·6	3·7	6·9	4·4

(2) Composition:—Copper, 82·8; lead, 4·1; tin, 6·9; zinc, 5·9 per cent.

Weight of alloy taken g.	Copper found Per Cent.	Lead found Per Cent.	Tin found Per Cent.	Zinc found Per Cent.
0·2500	82·9	3·9	6·9	6·0
0·2500	82·8	4·0	6·9	5·9
0·2500	82·9	4·0	6·9	6·0

(3) Composition:—Copper, 83·6; lead, 2·8; tin, 11·9; zinc, 1·3 per cent.

Weight of alloy taken g.	Copper found Per Cent.	Lead found Per Cent.	Tin found Per Cent.	Zinc found Per Cent.
0·2500	83·6	2·8	12·0	1·4
0·2500	83·7	2·8	12·0	1·3
0·2500	83·6	2·8	11·8	1·3

I wish to thank Dr. Sand for his interest in this work.

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THE SIR JOHN CASS TECHNICAL INSTITUTE
JEWRY STREET, LONDON, E.C.3

Studies in Internal Electrolysis, III

The Determination of Small Quantities of Silver in the Presence of various other Metals and its Application to the Analysis of Galena and Pyrites

BY JAMES G. FIFE, M.Sc., F.I.C.

COLLIN[1] has determined bismuth and copper in lead bullion and lead ores by internal electrolysis, using the apparatus described by Sand,[2] and Clarke, Wooten and Luke[3] have described the determination of small quantities of bismuth and copper in lead alloys containing antimony and tin by internal electrolysis, using an apparatus somewhat similar to that described by Sand, but neither Collin nor Clarke, Wooten and Luke determined the silver present.

Tutundžic[4] used a silver cathode in the determination of silver by internal electrolysis of a solution containing the silver as sulphate in presence of a little nitric acid. The anode was nickel, and the anolyte was a 2 per cent. solution of nickel sulphate slightly acidified with sulphuric acid. No stirring device was used.

Holland and Bertiaux[5] have described the separation of silver from copper by internal electrolysis of a sulphate solution at 70° C. They state that, unfortunately, the silver does not adhere well to the cathode. They prefer to precipitate the silver as silver chloride, to dissolve the precipitate in potassium cyanide solution, and to determine the silver electrolytically in a cyanide solution as in the method of Luckow. These authors also provide no means of stirring.

François[6] has also described a method for the determination of silver by internal electrolysis. The catholyte contained the silver to be determined in the form of a cyanide or nitrate, and the anolyte was the same as the catholyte with the omission of the silver. The anode was of zinc, and a platinum dish was used as cathode. No means of stirring was provided, and a filter-paper diaphragm was used to separate the anolyte and catholyte.

The apparatus used in the present investigation was that described by Sand,[2] with the modifications used in the determination of small proportions of cadmium and of nickel in zinc.[7] The anodes consisted of 18 S.W.G. copper wire.

DETERMINATION OF SILVER IN NITRIC ACID SOLUTION IN THE PRESENCE OF LEAD, COPPER AND BISMUTH.—It was found that small quantities of silver could be determined in the presence of large quantities of lead and small quantities of copper and bismuth by the method of internal electrolysis, provided that the catholyte contained sufficient nitric acid to keep the bismuth in solution.

Satisfactory results were obtained by the use of an anolyte containing copper nitrate equivalent to 1 g. of copper and 0·1 ml. of conc. nitric acid per 100 ml. and a catholyte, of approximately 300 ml., containing the silver to be determined (added as nitrate), lead nitrate equivalent to 10 g. of lead, 9 ml. of conc. nitric acid and varying quantities of copper and bismuth (both added as nitrate).

The results are shown in Table I.

In Expts. 3 and 9 the electrolysis was continued until constant weight was obtained, thus proving that a prolongation of the experiment has no harmful effect. With the apparatus employed it was found that a time of 30 minutes was sufficient, but when a new apparatus is set up the time required for solutions of known composition should be determined.

TABLE I

No. of expt.	Silver added g.	Copper added g.	Bismuth added g.	Silver found g.	Time of electrolysis Minutes
1	0·0025	0·0100	0·0100	0·0025	25
2	nil	0·0100	0·0100	nil	12
3	0·0005	0·0050	0·0050	0·0005	23
4	0·0015	0·0050	0·0050	0·0015	25
5	0·0050	0·0200	0·0200	0·0050	28
6	0·0070	0·0200	0·0200	0·0069	29
7	0·0085	0·0200	0·0200	0·0084	28
8	0·0100	0·0200	0·0200	0·0094	25
9	0·0100	0·0200	0·0200	0·0092	54
10	0·0080	0·0200	0·0200	0·0080	24
11	0·0090	0·0300	0·0200	0·0087	30
12	0·0015	0·0010	0·0010	0·0015	30
13	0·0025	0·0020	0·0020	0·0026	30
14	0·0045	0·0050	0·0050	0·0045	30
15	0·0065	0·0050	0·0050	0·0066	30

It appears from the results shown in Table I that about 8·5 mg. is approximately the upper limit of silver that can be determined by the method, but this is well above the limit usually found in 10 to 15 g. of galena.

The danger of using too little nitric acid is shown by the results given in Table II, in which in all the experiments only 4 ml. of conc. nitric acid were present in 300 ml. of catholyte, the conditions being otherwise as in the experiments in Table I.

TABLE II

No. of expt.	Silver added g.	Copper added g.	Bismuth added g.	Silver found g.	Time of electrolysis Minutes
16	0·0020	0·0100	0·0100	0·0021	30
17	0·0025	0·0100	0·0100	0·0028	30
18	0·0025	0·0100	nil	0·0027	33
19	0·0025	0·0100	nil	0·0025	25

It is thought that the high results in Expts. 16 to 18 were probably due to occlusion of bismuth hydroxide or other insoluble bismuth compound in the deposit, since, despite the fact that no bismuth was added in Expt. 18, there was probably a small amount of bismuth left on the diffusion shells from Expt. 17. This conclusion is supported by the result of Expt. 19, in which no bismuth was added and fresh diffusion shells were used.

In all the experiments in Tables I and II the temperature was about 60° C.

DETERMINATION OF SILVER IN AN AMMONIACAL SOLUTION IN THE PRESENCE OF COPPER.—It was found necessary to have the copper in the catholyte in the cuprous condition, since otherwise only about 50 per cent. of the silver added was deposited on the cathode, presumably owing to the greater part of the current available being employed in reducing the cupric ions to cuprous ions. In the anolyte, however, the copper should be in the cupric state, and it is desirable to have ammonium nitrate present. The following procedure gave satisfactory results:—The anolyte contained 0·1 g. of copper as cupric nitrate, 2 g. of ammonium nitrate and 3 ml. of ammonia (sp.gr. 0·880) per 100 ml. The catholyte (approximately 300 ml.) contained the silver to be determined (added as nitrate), 7 g. of sodium sulphite, 9 ml. of ammonia (sp.gr. 0·880) and varying amounts of copper (added as cupric nitrate). The catholyte solution was heated for a short time before the electrolysis until decolorised, and the electrolysis was carried out at approximately 70° C. It was found that there was a tendency to form a badly-conducting black deposit on the anodes, and it is therefore advisable to wash these with nitric acid after every second experiment, at least. The results are shown in Table III.

TABLE III

No. of expt.	Silver added g.	Copper added g.	Silver found g.	Time of electrolysis Minutes
20	0·0020	0·0200	0·0020	27
21	0·0040	0·0200	0·0039	22
22	nil	0·0200	nil	20
23	0·0050	0·0200	0·0049	26
24	0·0100	0·0200	0·0097	49
25	0·0010	0·0050	0·0010	30

APPLICATION OF THE METHOD TO THE DETERMINATION OF SILVER IN GALENA.*—The following procedure is recommended:—From 15 to 20 g. of galena are weighed and dissolved in nitric acid, an excess of about 9 ml. of the conc. acid being used, and the solution is boiled for about 30 minutes. A convenient method is to use the conc. acid diluted with about ten times its volume of water. The solution is then filtered, and the filtrate is diluted to about 300 ml. and electrolysed for 30 minutes at approximately 60° C., the anolyte described in connection with the experiments in Table I being used. The residue from the nitric acid extraction is further extracted for an hour at room temperature, with intermittent stirring, with 30 ml. of 10 per cent. potassium cyanide solution and about 60 ml. of water, and filtered. The filtrate is acidified with nitric acid and boiled to remove all hydrocyanic acid. It is important that all the hydrocyanic acid should be removed, since otherwise the results in the subsequent electrolysis will be low, probably owing to complex formation. The solution is neutralised with ammonia, treated with a further 9 ml. of ammonia (sp.gr. 0·880) and 7 g. of sodium sulphite, boiled for a short time, and filtered. The filtrate is then electrolysed for 30 minutes at approximately 70° C., the anolyte described in connection with the experiments in Table III being used.

Table IV gives results for two galenas—one from Matlock, Derbyshire (A), having a lead-content of 84·4 per cent., and the other an argentiferous galena of unknown origin (B) having a lead-content of 68·5 per cent.

The results by the usual method of fire assay were 0·0294 per cent. for galena A and 0·0222 per cent. for galena B.

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* The lead-content of the galena is conveniently determined by the method described by Collin.[8]

In Expt. 26, after the electrolysis in the nitric acid solution, 2 mg. of silver were added as silver nitrate, and the electrolysis was continued for a further 30 minutes. The weight of the additional deposit was 2 mg. Furthermore, the residue from the cyanide extraction was again extracted with cyanide, as described above, and the extract was filtered and treated in the same way as the first cyanide extract. No deposit was obtained after electrolysis for 30 minutes, thus showing that the first cyanide extraction completely extracted the residual silver. In Expt. 27 both electrolyses were continued until the weight was constant, and in Expt. 28 both silver deposits were removed with nitric acid, and the silver was determined gravimetrically as silver chloride. The amount found was 0·0068 g., equivalent to 0·0051 g. of silver, which agrees closely with the amount given in Table IV.

TABLE IV

No. of expt.	Galena	Wt. of galena taken g.	Silver found in nitric acid extraction g.	Silver found in cyanide extraction g.	Total silver Per Cent.
26	B	15·30	0·0005	0·0028	0·022
27	A	15·55	0·0017	0·0028	0·029
28	A	17·58	0·0030	0·0022	0·030

DETERMINATION OF SILVER IN SULPHURIC ACID SOLUTION IN THE PRESENCE OF COPPER, IRON, NICKEL, ARSENIC, AND ZINC.—It was found that small quantities of silver could be determined in the presence of large quantities of copper and iron and small quantities of nickel, arsenic and zinc by the method of internal electrolysis, provided that the iron was in the ferrous state. This can be ensured by the addition of hydrazine sulphate.

Satisfactory results were obtained by the use of an anolyte containing copper sulphate equivalent to 5 g. of copper and 0·1 ml. of conc. sulphuric acid per 100 ml.; and a catholyte of about 300 ml., containing the silver to be determined (added as nitrate), ferrous sulphate equivalent to 5 g. of iron, copper sulphate equivalent to 5 g. of copper, and varying quantities of sulphuric acid, nickel sulphate, zinc sulphate, sodium arsenite and hydrazine sulphate. The electrolysis was carried out at approximately 60° C.

The results are shown in Table V.

In Expt. 38 the electrolysis was continued until constant weight was obtained.

APPLICATION OF THE METHOD TO THE DETERMINATION OF SILVER IN CUPREOUS IRON PYRITES.—The following procedure is recommended:—A weighed quantity (about 20 g.) of the pyrites is heated on a sand-bath for about one hour with 20 ml. of conc. sulphuric acid and about 60 ml. of water, and after filtration the liquid is treated with 1 g. of hydrazine sulphate, heated to 60° C. and electrolysed for 30 minutes, the anolyte described in connection with Table V being used. The residue from the sulphuric acid treatment is extracted for 1 hour at room temperature with 30 ml. of 10 per cent. potassium cyanide solution and 60 ml. of water, with intermittent stirring. The mixture is filtered and the filtrate is acidified with nitric acid and boiled to remove all hydrocyanic acid. This is important, since otherwise the results in the subsequent electrolysis will be low (see p. 725). After removal of the hydrocyanic acid the solution is neutralised with ammonia, and a further 9 ml. of ammonia (sp.gr. 0·880) and 7 g. of sodium sulphite are added. The solution is boiled for a short time until decolorised, and then electrolysed for 30 minutes at approximately 70° C., the anolyte described in connection with Table III being used.

TABLE V

No. of expt.	Silver added g.	Nickel added g.	Arsenic added g.	Zinc added g.	Hydrazine sulphate added g.	Conc. sulphuric acid added ml.	Silver found g.	Time of electrolysis Minutes
29	0·0020	0·0100	0·0100	0·0100	0·4	3	0·0021	29
30	nil	0·0100	0·0100	0·0100	0·4	3	nil	26
31	0·0020	0·0100	0·0100	0·0100	0·4	12	0·0020	39
32	0·0020	0·0100	0·0100	0·0100	0·4	10	0·0020	25
33	0·0040	0·0100	0·0100	0·0100	0·4	10	0·0040	23
34	0·0010	0·0050	0·0500	0·0500	0·4	10	0·0010	20
35	0·0020	0·0050	0·0500	0·0500	0·4	14	0·0020	50
36	0·0040	0·0050	0·0500	0·0500	0·4	12	0·0040	35
37	0·0060	0·0100	0·0100	0·0100	0·2	10	0·0059	30
38	0·0090	0·0100	nil	0·0100	0·2	10	0·0087	33
39	0·0100	nil	0·0200	0·0200	0·2	10	0·0100	40
40	0·0005	0·0020	0·0020	0·0020	0·4	10	0·0005	30
41	0·0025	0·0050	0·0020	nil	0·2	10	0·0025	30
42	0·0045	nil	nil	nil	0·2	10	0·0045	30
43	0·0095	0·0200	0·0200	0·0200	0·2	10	0·0094	30

Results for a sample of cupreous iron pyrites (A) and the corresponding burnt pyrites (B) are shown in Table VI. (The cupreous iron pyrites was stated to contain about 43 g. of silver per metric ton (0·0047 per cent.).)

TABLE VI

No. of expt.	Pyrites	Wt. of pyrites g.	Silver found in acid extract g.	Silver found in cyanide extract g.	Total silver Per Cent.
44	A	21·62	0·0006	0·0004	0·0047
45	B	21·23	0·0005	0·0005	0·0047

In Expts. 44 and 45 both electrolyses were continued until the weight was constant.

I wish to thank the Rio Tinto Co., Ltd., for supplying the samples of pyrites, Mr. C. H. Holvey of the Metallurgical Dept. of this Institute, for carrying out the fire assays, and Dr. Sand for his continued interest in the work.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A COLORIMETRIC LIMIT-TEST FOR FREE ALCOHOL IN ESTERS, ETHERS OR KETONES

THIS method is a modification of Agulhon's test (*Bull. Soc. Chim.*, **1911**, **9**, 881; Abst., ANALYST, **1911**, **36**, 592) for alcohol in acetone. The strong aqueous nitric acid used by Agulhon is replaced by a 5 per cent. mixture of nitric acid in glacial acetic acid; this renders possible the extension of the method to ethers and esters immiscible with water, and greatly diminishes the likelihood of hydrolysis of esters.

The reaction is given by primary and secondary alcohols in general. In spite of this lack of specificity, however, it has been found useful in the analytical control of products manufactured from ethyl alcohol, in which no alcohols other than ethyl alcohol are likely to occur, and in which it is often required to determine rapidly whether the free alcohol content exceeds a limiting figure (*e.g.* esters and ether made from duty-free spirit, which are required by the Customs and Excise authorities to contain less than 2 per cent. of proof spirit). The method is not applicable to such readily-hydrolysed esters as ethyl oxalate, tartrate or lactate, nor to acetaldehyde.

QUALITATIVE TEST.—Five ml. of the sample are mixed with 10 ml. of a mixture consisting of 5 volumes of conc. nitric acid made up to 100 volumes with glacial acetic acid. This reagent should be freshly mixed. Potassium chromate (0·1 ml. of a 15 per cent. solution in water) is added, and the mixture is shaken. In complete absence of alcohols, the yellow colour persists practically unchanged, without developing any blue tint, for at least 30 minutes. In the presence of 0·5 per cent. of proof spirit in the sample, the colour is quickly changed to a clear blue.

QUANTITATIVE TEST.—In adapting the reaction as a quantitative limit-test, it is preferable always to compare the sample with controls made up from a purified stock of the compound under test. Esters and ethers may be sufficiently purified by repeated washing with brine. Acetone is best purified by distilling with an oxidising mixture (5 g. of potassium dichromate and 12·5 ml. of conc. sulphuric acid, made to 100 ml. with water) and redistilling from alkali. The purified stock should give a negative result in the qualitative test already described.

Five ml. of the purified stock are taken, and 0·5 ml. of aqueous ethyl alcohol of 20 per cent. proof strength is added. To a 5-ml. portion of the sample under test 0·5 ml. of water is added. To each are then added 10 ml. of the fresh nitric and acetic acid reagent, and then 15 per cent. potassium chromate solution (as nearly simultaneously as possible) 0·1 ml. at a time, shaking after each addition, until the sample retains a distinctly orange tint for several minutes. If the colour in the control is then still a clear blue, the alcohol in the sample is less than that in the control, *i.e.* less than 2 per cent. of proof spirit.

Where the limit is higher than this, a smaller quantity of the sample should be taken; for example, for a 5 per cent. limit, 2 ml. of the sample are sufficient. By using a range of controls containing 0·1–0·5 ml. of alcohol solution, with 0·4–0·0 ml. of water, a quantitative estimation of spirit within 0·2 per cent. of proof strength can be made.

I wish to thank the Government Chemist, Dr. J. J. Fox, for permission to publish this note.

E. G. KELLETT

GOVERNMENT LABORATORY
CLEMENT'S INN PASSAGE, LONDON, W.C.2

THE ANALYSIS OF MIXTURES OF METHANOL AND ETHANOL

In the course of some work on the slow oxidation of propane it was desired to analyse small quantities of a *dilute* solution of methanol and ethanol in water, in order to determine the two alcohols separately.

Although oxidation by acid dichromate has been widely employed for the determination of alcohol, and it has been observed that the acid concentration has a large effect on the rate of reaction, it does not appear to have been shown that by use of only a small concentration of acid the methanol is oxidised only as far as the formic acid stage. By two oxidations, the first being alcohol to acid and the second formic acid to carbon dioxide, both the total alcohols and methyl alcohol may thus be determined.

Procedure.—To about 20 ml. of the solution to be analysed, containing 0 to 5×10^{-4} g. mol. of alcohols, is added a measured excess of $N/5$ dichromate solution (*e.g.* 15 ml.) and 10 ml. of 10 per cent. sulphuric acid. The mixture is heated in a pressure-bottle in a steam-bath for about 25 minutes and then allowed to cool. The excess of dichromate is determined by adding a weighed amount of ferrous sulphate and then titrating back with dichromate, an external indicator being used. The amount of dichromate used in this oxidation is four equivalents per mol. of alcohol (either methyl or ethyl; the presence of propanol introduces an error, as it requires about five equivalents per mol.). If insufficient dichromate was used, a further quantity may be added and the heating repeated.

After this oxidation the solution contains formic and acetic acids from the alcohols. The formic acid is oxidised in a subsequent operation, a further quantity of dichromate being added (this need not be more than half the previous amount) and 10 ml. of conc. sulphuric acid. The mixture is refluxed for about 15 minutes, and then allowed to cool. After dilution and partial neutralisation of the acid the excess of dichromate is determined by adding potassium iodide and titrating the liberated iodine. The methyl alcohol originally present now requires two more equivalents of oxygen per mol.

If desired, the two oxidations may be carried out on separate aliquot parts of the mixture; the second portion should then receive 3/2 times as much dichromate as the first. The excess of dichromate after both oxidations may be determined iodimetrically, thus avoiding the inconvenience of the iron titration.

The following results are typical of those obtained; approximately $M/10$ solutions of the alcohols were used:

	Alcohol, ml.				Dichromate used in first oxidation ml.		Dichromate used in second oxidation ml.	
	Me.	Et.	Pr.	iso-Pr.				
(*a*)	3	1	0	0	15·4, 15·4	(16)	5·7, 5·65	(6)
(*b*)	3	0	1	0	17·1	(16)	5·5	(6)
(*c*)	3	1	0	1	16·4		6·1 [some acetone formed]	
(*d*)	1	1	0	0	7·6	(8)	1·7	(2)
(*e*)	5	0	0	0	20·1	(20)	10·0	(10)

The calculated figures are given in brackets.

A trace of isopropyl alcohol (*c*) does not greatly affect the results, as it requires only one equivalent of oxygen per mol.

E. J. Harris

Department of Chemical Technology
Imperial College of Science and Technology
South Kensington, S.W.7

THE RAPID DETERMINATION OF TRICHLOROETHYLENE VAPOUR IN THE AIR OF ROOMS

In 1933 a serious case of poisoning by trichloroethylene vapour discharged from a dry-cleaner's workshop was recorded in the Report of the Senior Medical Inspector of Factories and Workshops (Analyst, 1934, **59**, 626), and several other cases were described in the Report for 1935 (Analyst, 1936, **61**, 765). The question of the toxicity of trichloroethylene vapour was also discussed at an inquest in Birmingham (*cf.* Analyst, 1936, **61**, 97).

In the case that I have investigated, the staff of an office situated above a dry-cleaner's premises complained that the vapours that permeated the air of the room caused headache and other symptoms of illness, and I therefore devised the following rapid method of determining the amounts of trichloroethylene present. Approximately 30 litres of air from different parts of the room were passed at a uniform and regulated rate through an aspirator-bottle containing alcohol, an aliquot part by weight of the resulting alcoholic solution was burned in an ordinary spirit lamp, and the products of the combustion (hydrochloric acid, chlorine and phosgene, which is decomposed by water into hydrochloric acid and carbon dioxide) were collected in a standard solution of silver nitrate.

The apparatus consisted of a Pyrex boiling-tube having a side tube, 10 in. long and 5 mm. in internal diameter, about 1¼ inches from the closed end of the tube. The side tube was attached to the condenser by means of a rubber stopper. The lamp was placed below the mouth of the boiling-tube, its wick being adjusted to give a flame of about an inch high, and the combustion was continued for an hour.

It was found that 50 ml. of $N/50$ silver nitrate solution, divided between two scrubbers, were sufficient for small quantities of trichloroethylene, but for amounts exceeding 0·1 g. $N/10$ silver nitrate solution was used, and subsequently titrated with $N/10$ or $N/50$ potassium thiocyanate solution. The following results were obtained with the air of the room under investigation:

Air aspirated litres	Weight of alcoholic solution in spirit lamp g.	Alcoholic solution burned off in 1 hour g.	Chlorine calculated to trichloroethylene
24	38·8980	22·3200	1·95 mg. = 2·30 mg. per cb.ft. of air
33	20·4264	19·2670	2·23 mg. = 1·91 mg. per cb.ft. of air

In test experiments, in which quantities of 0·025 to 0·1 ml. of trichloroethylene (97 per cent. pure by the Carius method) were dissolved in alcohol and aliquot parts of the solution were burned in the lamp, the amounts recovered ranged from 90·07 to 92·88 per cent., or about 94 per cent. of the theoretical amount.

In connection with the determination of trichloroethylene in air, reference may be made to the colorimetric method of Barrett (*J. Ind. Hyg. and Toxicol.*, 1936, **18**, 341), which is based on a reaction described by Fujiwara (*Sitzungsb. u. Abhandl. Naturfors.*, Rostock, 1914, **6**, 33), who found that when a chlorinated hydrocarbon containing 3 carbon atoms is highly diluted with water and heated with sodium hydroxide and pyridine a colour is produced. Barrett found that the results were accurate to within ± 11 per cent., and that the method was capable of detecting 20 p.p.m. of trichloroethylene in air (0·7 mg. per cb. ft.).

In the thermal method of Olsen, Smyth, Ferguson and Scheflan (*Ind. Eng. Chem., Anal. Ed.*, 1936, 260; Smyth, *id.*, 379) air containing the chlorinated hydrocarbon is passed through a heated tube, and the products of the decomposition are absorbed in sodium hydroxide solution containing alcohol or a trace of saponin. After reduction of hypochlorite with sulphite the chloride is titrated with standard silver nitrate solution.

I have to thank Professor Cumming for his assistance in the work, and also Mr. A. F. Buchanan, my chief assistant, for making the tests.

City Analyst's Laboratory
140 Perth Road, Dundee
Andrew Dargie

EXAMINATION OF PRECIOUS STONES BY MEANS OF THEIR FLUORESCENCE IN ULTRA-VIOLET LIGHT

In a paper on the examination of precious stones (Abst., ANALYST, 1937, p. 767) Bolman refers to the application of fluorescence analysis in ultra-violet light, but gives no examples, and in view of this and of the general lack of information on this branch of the subject, the following notes may be of interest. They are selected from tests made during the past two years on authentic samples representing 30 different types of precious and semi-precious stones, and the examples given below are intended to show how the method may be of use to distinguish stones which (except, of course, to the expert) appear alike.

A synthetic aquamarine is sometimes confused with genuine Burma sapphire, but may be distinguished by its dull pink fluorescence, the latter stone appearing dark purple or black, and in this respect indistinguishable from the synthetic sapphire.

White topaz, white zircon and diamond also appear alike in daylight, but have a dull purple, pale mustard-yellow and mauve to black fluorescence, respectively. The method fails to distinguish diamond from paste, but true diamonds show various shades of purple or mauve, presumably according to the method of cutting used (*cf.* Bolman, *loc. cit.*).

Opal ("whiteclyffe") has a fluorescence similar in colour to that of an egg-shell, the characteristic green fire and orange-yellow colour seen in daylight being invisible, and this easily distinguishes it from moss agate, which is grey with a blue streak. Black opals have no fluorescence, and Mexican fire opals appear dull purple, but both of these stones are easily recognised by the unaided eye.

Chinese jade, amazonite, soudée emerald (beryl type) and chrysophane also resemble one another, and the fluorescence effects, though similar, are distinguishable, being dark green with bright streaks, dirty pale green, very dark green and pale opalescent green, respectively.

Finally, the brilliant, fiery deep-red fluorescence of the synthetic ruby readily distinguishes it from the paler and more pink red of the genuine ruby.

Other fluorescence colours which may be of interest (although the stones concerned are easily recognised without their aid) are as follows:—Genuine and imitation amethyst, mauve to black and mustard-yellow, respectively; blue and yellow sapphire, pink and orange, respectively (*cf. supra*); red and blue zircon, dirty red and dirty yellow, respectively; yellow and white topaz, dirty yellow-brown and dull purple, respectively; peridot, garnet, carnelian and turquoise, dark brown-green, dull purple, dull purple and mouse-grey, respectively.

JULIUS GRANT

HACKNEY TECHNICAL INSTITUTE
LONDON, E.

THE DETECTION OF CITRIC ACID, TARTARIC ACID AND CREAM OF TARTAR IN THE PRESENCE OF SUGAR

SOME difficulty has been experienced in eliminating all traces of sugar when testing lemonade powder for tartrate by means of the resorcinol and sulphuric acid test. The charring of even a trace of sugar is sufficient to mask the red colour produced in the test. Repeated crystallisation of the tartrate as potassium hydrogen tartrate from alcohol does not overcome this difficulty. The following procedure, which depends upon the solubility of citric and tartaric acids in ether (*cf.* Elsdon and Lees, ANALYST, 1933, 58, 323), has therefore been evolved.

(1) CITRIC AND TARTARIC ACIDS.—Shake 5 g. of the sample in a test-tube with 10 ml. of methylated ether and, after about 1 minute, filter into a small flask. Evaporate off the ether, and to the residue add about 1 ml. of water. Test 2 or 3 drops of this solution for tartaric acid by the resorcinol and sulphuric acid test.

Wash the rest of the solution in the flask into a boiling-tube with a few ml. of water and test for citric acid by the mercuric sulphate and potassium permanganate test. The solubility of these acids in ether is sufficient to give a good positive reaction.

(2) CREAM OF TARTAR.—If there is a negative or only a slight positive reaction for tartrate by the test described above, the following test should be applied:—Shake the same portion of the sample with 10 ml. of acidified ether (1 drop of dilute sulphuric acid in 20 ml. of ether) and proceed as before. In the presence of cream of tartar a good positive reaction will be obtained.

It should be noted that in the absence of cream of tartar a slight pink colour followed by charring may result from the action of the acid on the sugar. (For this reason the amount of acid used must not exceed that indicated.) The intensity of this colour, however, is in no way comparable with that obtained with cream of tartar, and if a control test with cream of tartar is made no doubts should arise.

R. DE GIACOMI

11 BILLITER SQUARE,
LONDON, E.C.3

A ROUTINE TEST FOR THE DETECTION OF HIGHLY HARDENED OILS AND MUTTON AND BEEF FATS IN BUTTER AND GHEE

HIGHLY-HARDENED oils, as do mutton and beef fats, contain a much higher proportion of the glycerides of stearic acid than do butter and ghee. These glycerides are only sparingly soluble in alcohol at room temperature (about 30° C. in Madras), whereas they dissolve readily in acetone. Thus, by using a suitable mixture of alcohol and acetone it is possible to dissolve practically all the glycerides in a fat, except those of stearic acid, and by treating a definite quantity of butter-fat or ghee with specified proportions of such a mixture, one can ascertain whether a given sample contains more stearic acid glycerides than are present in genuine butter-fat or ghee, allowance being made for abnormal variations in the stearic acid content of some butters.

METHOD.—The butter-fat or ghee under examination is filtered through a dry No. 4 Whatman filter-paper into a 30-ml. beaker maintained at 60° C. in an air-oven. One ml. of the clear melted fat is run into a test-tube, about 16 cm. long and 16 to 18 mm. in diameter, 30 seconds being allowed for the pipette to drain. Fifteen ml. of a mixture of acetone and alcohol (650 ml. of pure dry acetone made up to 1 litre with absolute alcohol) are added, and the test-tube is warmed, shaken and closed with a rubber stopper. It is then left for 3 hours in a water-bath maintained at 30° C. (±0·1° C.), after which it is removed, without shaking, and examined by transmitted light. Even the slightest deposit of crystals is a definite indication of the presence of mutton or beef fat or of a hardened oil.

A clear solution does not necessarily indicate that the sample is genuine, but it shows that there has not been any material adulteration with these types of fat. If the admixture is considerable, very heavy deposits are obtained, the quantity of crystals varying with the nature of the adulterant. A rough quantitative idea of the amount of stearic acid glycerides can be formed by repeating the test with 1 ml. of the fat and different volumes of the solvent, say, 5, 10, 20 and 25 ml.

Most genuine butter-fats do not yield crystals, even with 5 ml. of the solvent; a few give them with 5 ml., but not with 10 ml.; only in one instance did an abnormally hard butter-fat give crystals with 10 ml., and even this sample failed to give them with 15 ml. Hence 15 ml. may safely be taken as the limiting volume. Mutton fat, beef fat and hardened fish oils gave crystals even with 40 ml. of the solvent.

The method has the advantage that it is independent of the Reichert–Wollny value. For example, the genuine hard butter-fat mentioned above, which had a

Reichert-Wollny value of 18·9, gave crystals with 5 and 10 ml. of solvent, but not with 15 ml., whilst a heavily adulterated sample, with a Reichert-Wollny value of 19·1, gave a very large deposit of crystals with 15 ml.

A mixture of 80 per cent. of a genuine butter-fat (no deposit with 5 ml.) with 20 per cent. of hardened whale oil yielded a slight deposit of crystals with 15 ml. of the solvent.

A series of comparative experiments showed that the conclusions to be drawn from this test and from the Ave-Lallemant baryta values are the same, except that the present test is applicable only to the hard fats.

In general, samples giving a positive result in the acetone-alcohol test also give high "titres" for the insoluble fatty acids, although there are exceptions. A high stearic acid content accompanied by a comparatively high oleic acid content in the insoluble fatty acids would give a low "titre," although the crystals obtained may give a definite indication of adulteration, as oleic acid does not interfere with the present test. For example, an adulterated sample of butter, which gave a titre test of 40·5° C. (*i.e.* well within the range of genuine samples, which have given titre values up to 42·0° C.), yielded a slight deposit of crystals with 15 ml. of the solvent.

My thanks are due to Mr. Herbert Hawley, Government Analyst, Madras, for his suggestions and help during the investigation. V. VENKATACHALAM

THE CORPORATION LABORATORY
WATER WORKS, KILPAUK
MADRAS

Sussex Ground Oats

WE have been requested by the Ministry of Agriculture and Fisheries to give publicity to the following communication, dated August 27th, 1937:

"At a recent meeting of the Standing Advisory Committee set up under Section 23 of the Fertilisers and Feeding Stuffs Act, 1926, to advise the Minister with respect to the regulations under that Act, consideration was given to the subject of 'Sussex ground oats,' and it was decided to advise the Department that, in the opinion of the Committee, 'Sussex ground oats' should conform to the definition of 'ground oats,' as stated in the Fourth Schedule of the Act, *i.e.* 'the meal obtained by grinding commercially pure oats as grown'."

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY OF DERBY

ANNUAL REPORT OF THE COUNTY ANALYST

THE total number of samples of food and drugs examined was 2071, of which 1356 were purchased formally and 715 informally.

FLUORINE IN DERBYSHIRE WATERS.—The question of fluorine in Derbyshire waters, to which reference was made in the Report for 1935 (ANALYST, 1936, **61**, 837), has continued to receive attention in the County Laboratory, and so far 43 waters have been examined. The results were as follows:—Waters free from fluorine, 9; containing 0·1 p.p.m., 11; 0·2 p.p.m., 7; 0·3 p.p.m., 5; 0·4 p.p.m., 3;

0·5 p.p.m., 2; 0·6 p.p.m., 1; 0·7 p.p.m., 3; 0·8 p.p.m., 1; 1·4 p.p.m., 1. Thus only one water contained fluorine in excess of 1 p.p.m., as found by American workers in waters in areas affected with fluorosis. The occurrence of "mottled teeth" in the Maldon district was found by Ainsworth (ANALYST, 1934, 59, 380) to be associated with waters containing 4·5 and 5·5 p.p.m.

SUSSEX GROUND OATS.—An increased number of samples has been taken in an attempt to suppress the adulteration of this article. Ten samples were found to be adulterated, the usual adulterants being barley, wheat and rye, or mixtures of these, together with additional oat husk. One sample contained 25 per cent. of rye and 25 per cent. of added oat husk, and another 40 per cent. of added oat husk and 10 per cent. of rye, wheat and barley. R. W. SUTTON

CITY AND COUNTY OF KINGSTON-UPON-HULL

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1936

OF the 2148 samples of food and drugs submitted by the inspectors, 1388 were formal and 760 informal.

TALC ON RICE AND SPLIT PEAS.—Two samples of rice (from one source) and six samples of split peas (from three retailers) were faced with talc in amounts varying from 0·1 to 0·35 per cent. In the Report of the Local Government Board (No. 8, 1909; ANALYST, 1909, 34, 430) an outside limit of 0·5 per cent. of talc was suggested as sufficient to meet the requirements of traders. Since then it has become increasingly evident that not only is the practice unnecessary, but that it is also ineffective for its intended purpose of combating the attacks of weevils. In 1910 the Hull Corporation issued a warning against the practice, and until recently the sale of "faced" rice in the city had almost ceased. Pearl barley and lentils have also been found from time to time to be faced with talc. All the vendors of these eight samples have been notified of the Corporation's objection to this addition to food, and most of the wholesale firms concerned have signified their desire to comply with the notification.

"DEVON CREAM" TOFFEE.—Two samples bearing this label were returned as adulterated, since they contained 15 per cent. of fat (mainly coconut oil) and not more than 1 per cent. of butter-fat. The makers were asked to cease using the description of "Devon Cream," and intimated their intention of immediately withdrawing their stocks of this toffee in the city.

ALLEGED POISONING WITH COPPER DUST.—The case of a man whose work brought him into contact with copper dust, which was alleged to be the cause of his illness, involved numerous determinations of this metal. During his life, the urine, hair and blood (five samples) were examined for copper (and arsenic) and about twice the normal figure was present in the blood (namely, 4 to 4·2 parts per million).* The urine showed 0·8 p.p.m. of copper; the hair and urine were free from any significant amount of arsenic. After death, the liver of this man was found to contain 3·3 p.p.m., and the bone (tibia) 2·0 p.p.m. of copper, which appear to be within normal limits. A verdict of death from natural causes was returned at the coroner's inquest.

SODIUM NITRITE POISONING.—Another case was one of suicide with sodium nitrite. Seven articles were submitted for examination. Post-mortem, all the organs (stomach, intestines, liver and kidney) were found to be bright red in colour, and the presence of nitric oxide haemoglobin in the blood was proved. An almost empty bottle, on the sides of which were a few adherent crystals, was found to contain sodium nitrite, and it would appear that the deceased had possibly taken about 100 grains of this salt. The stomach-contents, and a cup and saucer, all showed evidence of the presence of appreciable amounts of sodium nitrite. It is to be noted that this substance (included in the British Pharmacopoeia) is one of the very few ordinary salts which is given medicinally and has a comparatively small medicinal dose (maximum, two grains). Sodium nitrite must therefore be considered to be an active and potentially poisonous substance, especially when taken in appreciable amount in one dose. (*Cf.* ANALYST, 1936, 61, 614, 685; 1937, 740.)

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* The "normal" figure for copper in human blood was taken from the results recorded by McFarlane (*Biochem. J.*, 1932, 26, 1022). The authorities prior to McFarlane gave 0·075 to 0·114 mg. Cu per 100 ml. (= 0·75 to 1·14 p.p.m.). McFarlane found by his method 0·185; 0·170; 0·181; 0·210 mg. Cu per 100 ml. of the blood (1·70 to 2·10 p.p.m.). Thus our samples (two) of blood from one case, taken at different times, contained approximately twice McFarlane's average normal figure for human blood.

Tompsett (*Biochem. J.*, 1934, 28, 2088) states that normal human urine contains from 0·08 to 0·48 parts Cu per million. Our sample contained 0·8 part, and according to Tompsett the amount was probably somewhat high.

ARNOLD R. TANKARD

Department of Scientific and Industrial Research

THE CAUSES OF STAIN AND DECAY IN IMPORTED TIMBER*

THE discoloration of timber is due to (i) chemical and (ii) biological causes.

CHARACTERISTICS OF CHEMICAL STAINS.—Stains due to chemical causes are usually distributed in spots or irregular blotches which bear no relation to the grain of the wood, and the colour may be rust-red, black, blue or grey. Iron stain in woods containing tannin is correctly described as "ink stain." Stains due to oxidation of wood constituents occur in some white timbers, such as sycamore, and may be distributed over the whole exposed surface. Pink and brown stains due to chemical oxidation may be distinguished from fungal stains by their uniform distribution. Water stains, due to drip or to floating the timber in water, leave a "tide mark" owing to deposition of dirt, etc., on drying.

STAINS CAUSED BY DECAY FUNGI AND BY SAP-STAIN AND MOULD FUNGI.—It is important to establish whether the fungus producing a stain is one that causes decay or one of the sap-stain type. Decay fungi attack the actual structure of the wood, whereas the sap-stain fungi and the moulds feed on the contents of the cells and do not appreciably affect the mechanical properties of the wood. The main distinctions between stain and decay may be summarised as follows:

Stain	Decay
Mostly confined to sapwood.	Not confined to sapwood.
Colour:—Blue, blue-grey or green—occasionally pink or yellow.	Colour:—Dark brown or reddish-brown, often occurring in streaks.
	In advanced stage, cracking evident.
	White pockets or streaks in timber attacked by white rots.
No appreciable weakening of timber observed when the fibres are raised with a knife.	Fibres break off short when raised with the point of a knife.
	Black or coloured zone lines present.

SAP-STAIN.—The best known example is the blue-grey discoloration of the sapwood of coniferous timber (blue stain), but fungal staining is also of common occurrence in many hardwoods, such as poplar and ash. Pink and yellow tints are not infrequently produced by mould fungi in softwoods. In mild cases the spots or flecks are confined to the surface, but more usually the discoloration is in streaks or bands running parallel with the grain, or in severe cases the whole sapwood may become blue or blackish grey. Microscopic examination of blue-stained timber shows numerous brown hyphae of the fungus, which are usually most frequent in the medullary ray cells. Sap-stain usually occurs only in timber containing moisture above 20 to 25 per cent. (calculated as a percentage of the oven-dry weight). Green, yellow or pink mould growth on the timber indicates that conditions are damp, but does not necessarily mean that the timber itself is discoloured.

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* Forest Products Research Records, No. 18 (*Mycology Series*, No. 2). By K. St. G. Cartwright, M.A. H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 6d. net.

DOTE AND DECAY.—Dote is defined as localised patches or pipes of incipient decay, as distinguished from the actual decay of timber caused by fungi or other agents. The attacked wood usually becomes either darker or lighter than normal. With a brown rot the first indications of attack are streaks or patches of brown or reddish brown; with a white rot (*e.g. Fomes annosus*) the wood becomes abnormally pale and sometimes shows small white pockets. Sometimes the heartwood shows bands of purplish pink, but this must be distinguished from the general, even, uniform purple-pink that may be observed in certain species of softwoods, *e.g.* Douglas fir. If the wood is abnormally pale in colour and has a mottled appearance, or shows light-coloured streaks or pockets, it is probably affected by decay. The presence of dark irregular contour-like lines also indicates decay.

Infection by a decay fungus may have been already present in the standing tree, or it may have been introduced after felling and conversion. Decay develops much more slowly than sap-stain and mould, and even under optimum conditions no appreciable growth is likely to take place under four weeks, and usually six months have to elapse before the timber becomes markedly affected.

When once timber has been dried as a whole to an average moisture-content below 20 to 25 per cent., it will be immune from fresh development of sap-stain and mould, and no spread of decay is likely. Below a temperature of 40° F. the growth of most fungi is slow, and no growth will take place below about 35° F.

INDICATIONS OF CAUSE OF DAMAGE.—Moisture in timber converted soon after felling is fairly evenly distributed throughout, but as the timber dries, the surface will lose moisture more rapidly than the interior. Hence, under normal conditions some indication of a moisture gradient can be detected for a considerable time. If the timber was shipped in an unseasoned condition, the moisture-content in the centre will be higher than that of the outer parts, and responsibility for the development of the stain must, in the main, be placed prior to shipment. A fairly accurate opinion can usually be formed from the extent and depth of staining; but where stain or active mould is confined to the surface it shows definitely that surface moisture is present. By moisture determination it is, as a rule, possible to determine whether this surface moisture is due to the movement of moisture from the interior of imperfectly seasoned timber, to water from the exterior, or to both.

If the mould growth is dry and the moisture-content reasonably low, it is probable that the timber was sufficiently re-wetted after shipping to allow of surface stain and mould growth, but that afterwards it had dried and further development had been arrested.

Stain that is deep seated and fairly uniform in distribution almost invariably suggests that the timber remained close piled in an unseasoned condition for at least two or three weeks. Extensive internal decay usually indicates that the original infection occurred in the standing tree, and has developed further owing to storage under unsuitable conditions. A white pocket-rot in softwoods also almost invariably points to infection in the standing tree.

Rot that is more or less confined to the sapwood indicates infection after felling, and a judgment as to when it occurred has to be based on the extent of the trouble. It is comparatively rare for decay to increase to any great extent during the course of a voyage. If fungal growth is visible on the surface, but decay is entirely superficial and the moisture-content is high on the surface yet lower in some part of the interior, there is some justification for considering that infection may have occurred on the ship or that the surface of the timber had become very moist before shipment, thus encouraging the development of any fungus spores present on the timber.

Prevention of Deterioration of Timber in Transit.—The development of stain or decay can be prevented by seasoning the timber to a moisture-content below 20 to 25 per cent. of its oven-dry weight, and protecting it against subsequent re-wetting. Since, for economic reasons, it is not always possible to season the lower grades of timber to the safety-point before shipment, it is necessary to dip such timber in an antiseptic bath immediately after sawing.

Preparation of Wood Sections for Microscopic Examination.—Since most of the decay fungi have colourless hyphae, longitudinal sections of the wood should be stained when decay is suspected. The following simple method is recommended:—(i) Stain the section for 30 seconds to 1 minute in a 1 per cent. solution of safranin; (ii) wash with water; (iii) stain in picro-aniline blue (25 ml. of saturated aniline blue solution plus 100 ml. of saturated aqueous picric acid solution) by covering the section with the stain and warming gently until the liquid begins to simmer; (iv) wash with water until all unfixed blue has been removed; (v) wash in 95 per cent. alcohol and finally in absolute alcohol; (vi) clear in clove oil, and mount in Canada balsam if permanent preparations are required.

By this method the lignified walls of the wood cells are stained red and the fungus hyphae clear blue. In non-lignified tissues or badly decayed areas the wood may be stained blue, but even so the hyphae are usually quite apparent.

Appearance of Hyphae.—*Decay fungi.*—The presence of large bore holes in the cell walls caused by the penetration of the hyphae is characteristic of most of the species of wood-destroying fungi, whereas many of the staining fungi produce minute bore holes. Some species of decay fungi (*e.g.* the white pocket rot fungus, *Trametes pini*) may form small bore holes, but the hyphae passing through such bore holes do not show pronounced constriction, as is usually seen in fungi that produce blue stain. Another distinguishing feature is the presence of the so-called clamp connections in wood-destroying fungi, and cross-walls (septa) are not so frequent as in sap-stain fungi.

Sap-stain fungi.—The hyphae of sap-stain fungi are usually brown, although the fine young hyphae may be colourless. The brown hyphae are large and have many cross-walls; they are not stained blue. Some of the wood-destroying fungi have coloured hyphae, but, as a rule, they are of a golden brown or yellow tint and have few septa. The bore holes of staining fungi are small and the hyphae are constricted where they pass through a cell wall. Clamp connections are never present on the hyphae.

Fruit and Vegetable Preservation Research Station, Campden

ANNUAL REPORT, 1935–1936*

The activities of the Station during the year have again been closely connected with the solution of practical problems, and close contact has been maintained with commercial practice through the Technical Advisory Committee and through the section of the advisory work concerned with canners' problems. Among the more recent developments special attention may be called to an investigation into the nutritional value of canned foods, which is being made in collaboration with the Rowett Research Institute, Aberdeen. This is the first Report of the Station under the control of the new Management Committee (*cf.* Analyst, 1936, 61, 694).

Varieties of Fruits—Canning Trials.—The Canners' Bulletin, entitled

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[*] Published by the University of Bristol, 70 pp. Introduction by F. Hirst, M.Sc. (Director), and Contributions by T. G. Gillespy, G. Horner, W. B. Adam and G. S. Sidappa, and W. B. Adam and J. Stanworth.

"Varieties of Fruits for Canning," was completely re-written, and now includes the results of the canning trials conducted at Campden between the years 1925 and 1935, together with tables showing the relationship between cross-sectional diameters and weights of stone fruits and gooseberries.

GROWTH OF MIXED ORGANISMS IN CANNED VEGETABLES.—Experiments in the United States have shown that bacteria may be drawn through the seams of cans, even when leaks could not be detected by any known physical tests. A test was therefore devised in which suspected cans were filled with dextrose nutrient broth, exhausted, and sealed with a plate soldered over the hole through which their contents had been emptied. They were then retorted at 112° C. for 25 minutes after which the retort was brought to atmospheric pressure in three minutes, and the cans were cooled in water which had been heavily contaminated with strains of bacteria originally isolated from the cans. All the cans proved to be sterile, showing that, if leakage had been the cause of spoilage, the seams had since become stable.

New Method of Inoculating Cans.—To prevent contamination by the inrush of air when the can is punctured, the following method has been devised. A small round depression is made in the centre of one end of the can, which is then washed, and the top is wiped over with alcohol. This is burned off, and 1 to 2 ml. of the inoculating material is pipetted on to the can over the depression. The can is then pierced by means of a gramophone needle, previously tinned with solder and fixed in a holder consisting of an iron rod with a hole bored longitudinally in one end. The needle and the end of the holder are sterilised in a flame, the point of the needle is placed in the depression on the top of the can, and the holder is given a light blow sufficient to pierce the can. The needle then acts like a valve, but by moving it slightly the pressure is released a little, and the inoculum is drawn into the can. The pressure of the hand is then released, and an assistant at once smears flux round the needle and solders it in place, sealing the puncture. The holder is then drawn off the needle. Control tests are made with sterile water instead of the inoculating material.

Growth of Cultures in Cans.—When only spore-forming bacteria—often of a single type—are isolated from a can it is probable that the spores have survived the sterilisation process. On the other hand, the isolation of mixed cultures of non-heat-resistant types, often including coccus forms, points to leakage of the can after processing. From the results of a series of experiments, described in detail in the Report, the conclusion is drawn that there is no danger of the heat-resistant sporing bacteria masking the presence of non-heat-resistant short rod types. The reverse seems to be more likely.

MINERAL-CONTENT OF CANNED VEGETABLES.—The results so far obtained indicate that a considerable loss of the important mineral salts of vegetables occurs in the course of home-cooking and canning, and if the drained weight of vegetables is considered, the losses for these two processes are of approximately the same magnitude. It is noteworthy that the losses on blanching are smaller, though still of importance, and if the drained liquid from canned vegetables can be utilised, the net loss will be equal to the loss on blanching, thus emphasising the gain in nutritional value obtained by utilising the covering liquid.

COMPOSITION AND TEXTURE OF DRIED PEAS.—Chemical analyses of the various samples of peas connected with field trials (described) show that there does not appear to be any direct relationship between the figures obtained and the observed differences in the texture of the canned product, with the possible exception of that associated with the phosphate-content of the ash, or the ratio of phosphate to calcium oxide.

Treatment with artificial fertilisers does not influence the texture appreciably, and this is further borne out by manurial trials conducted in 1936. The evidence at present available points strongly to the fact that variation in texture is mainly governed by the rate at which the peas dry in the field, and further tests are being planned along these lines.

ACIDITY AND HYDROGEN ION CONCENTRATION OF CANNED FRUITS.—About 400 determinations have been made in studying the question of the variability of *p*H and acidity in English canned fruits. The following table summarises values obtained for each class of fruit:

ENGLISH CANNED FRUITS

	No. of samples tested for		*p*H		Acidity (as citric acid)	
Fruit	*p*H	Acidity	Average	Range	Average Per Cent.	Range Per Cent.
Purple plums	10	6	2·79	2·69–2·89	1·25	1·09–1·36
Loganberries	29	13	2·92	2·70–3·34	1·29	0·98–1·55
Golden plums	25	13	2·93	2·80–3·09	1·01	0·88–1·10
Victoria plums	18	9	2·95	2·83–3·07	0·76	0·62–0·85
Gooseberries	32	18	2·96	2·72–3·16	1·15	0·97–1·43
Apples (solid pack)	8	8	2·96	2·84–3·14	0·68	0·44–0·97
Damsons	21	10	3·02	2·91–3·16	1·39	1·11–1·59
Blackberries	19	17	3·02	2·81–3·40	1·03	0·70–1·44
Raspberries	35	15	3·05	2·78–3·46	0·83	0·84–1·24
Blackcurrants	22	11	3·10	2·82–3·47	1·64	1·30–2·02
Greengages	16	14	3·17	2·96–3·36	0·78	0·62–0·97
Cherries (acid)	11	10	3·23	3·03–3·39	0·86	0·61–1·14
Cherries (sub-acid)	5	4	3·30	3·24–3·34	0·80	0·76–0·85
Strawberries	45	22	3·46	3·16–3·76	0·47	0·38–0·71
Cherries (sweet)	25	20	3·86	3·63–4·31	0·25	0·16–0·35

Most of the tests on the juice of fresh fruits indicated that the range of *p*H during ripening is less for plums than for soft fruits, and this may account for the wider range in values shown in this table.

Some of the results obtained with imported canned fruits are shown in the following table:

IMPORTED CANNED FRUITS

Fruit		*p*H range	Acidity (as citric acid) Per Cent.
Grapefruit	(20)	3·16–3·49	0·61–1·35
Bilberries	(3)	3·00–3·60	—
Peaches	(5)	3·43–3·91	—
Apricots	(5)	3·51–3·79	—
Pears	(5)	3·62–4·33	—
Pineapples	(24)	3·41–4·30	0·21–0·75
Muscat grapes	(5)	3·44–3·76	0·20–0·36
Quinces	(1)	3·34	0·39
Cape berries	(3)	3·76–3·86	0·88–0·97
Mandarin oranges	(2)	3·80–3·84	0·55–0·58
Nectarines	(3)	3·96–4·07	0·20–0·37
Guavas	(6)	3·98–4·28	0·19–0·33
Mangoes	(14)	3·43–4·69	0·12–0·61
Litchis	(7)	4·09–4·39	0·20–0·29
Tomatoes	(5)	4·38–4·56	0·30–0·50
Rambutans	(3)	4·78–4·81	0·19–0·20
Papaws	(5)	4·68–5·21	0·03–0·07
Loquats	(2)	4·93–5·36	0·01–0·02
Figs, fresh	(1)	5·17	0·39

EFFECT OF INTERNAL PRESSURES ON THE VOLUME OF THE CAN.—Under normal conditions of closing and processing any of the standard sizes of cans the permanent strains set up are very slight, but it sometimes happens that excessive pressures develop during processing, and these may prevent the cans from returning to their original shape when cool. The cylindrical part being relatively rigid and the ends flexible, the latter tend, as they are stretched, to take the form of a section of a sphere. The effects of this action may be noticed after the ends have been drawn in, by the raising of the level of the bead (*i.e.* the main raised ring) and by a slight lifting of the level of the horizontal part of the countersink. These strains appear to take place before the end seams are seriously disturbed, and it is possible that a study of their magnitude may be helpful in diagnosing the cause of certain types of seam trouble. This work is still in progress.

Government of Madras

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1936

IN the absence of Lt.-Col. Clive Newcomb, the Report has been drawn up by the Acting Chemical Examiner, Mr. S. Rajagopal Naidu, F.I.C. As usual, it is largely concerned with cases of poisoning. In 1936 there were 365 cases of human poisoning, opium heading the list with 31 cases, closely followed by oleander, with 29 cases. There was an increase in cases of madar juice poisoning (14, as compared with 5 in 1935). Among other points of toxicological interest reference is made to the following:

Nitrite Poisoning.—One case of suicide with sodium nitrite and one with potassium nitrite were investigated. In the former, nitrite equivalent to about two-fifths of a grain was detected in the viscera; in the latter, nitrite equivalent to about 4 grains of potassium nitrite was found in the stomach, whilst the urine in the bladder contained about 111 p.p.m. of potassium nitrite and the vomit 144 grains. The kidneys were normal, the peritoneum contained about 6 ozs. of dark blood and fluid, and the mucous membrane of the stomach and intestines showed congestion with bright red patches (*cf.* p. 735).

MADAR JUICE POISONING.—All the cases were fatal. The post-mortem appearances in 13 of the cases may be summarised as follows:

In three cases the face was bloated. In six cases there was bloody discharge from mouth and nose. There was congestion of the lungs in eight cases, of the liver in six, of the spleen in four, of the kidneys in seven, and of the membranes of the brain in six cases. There was congestion of the inner surface of the stomach in four cases, of the outer surface only in three, and of part of the inner and the outer surface in one case; the stomach and intestines were normal in the other five cases. Of the eight cases showing congestion of the stomach, six showed congestion of the intestines, whilst the intestines in the remaining two cases were normal. The mode of death was asphyxia with gastro-intestinal irritation in six cases, asphyxia alone without any gastro-intestinal irritation in two, gastro-intestinal irritation alone without asphyxia in two, and syncope without asphyxia or gastro-intestinal irritation in three cases. Four of the cases of asphyxia, one of the cases of gastro-intestinal irritation, and one of the cases of syncope showed a co-existent cerebral irritation.

The juice, which is used by local application as an abortifacient, has sp.gr. about 1·021, and contains about 14·8 per cent. of total solids. It has an acid reaction, and when left for some time, separates into a white coagulum and a clear straw-coloured serum which contains about 3 per cent. of total solids and about 0·7 per cent. of mineral matter. The exact nature of the organic acid or acids in madar juice has not been determined, but the ethyl ester or esters have a distinctive odour.

An alkaline alcoholic extract of the coagulum when treated with petroleum spirit yields a white crystalline extract identifiable by its colour reactions, and by the fact that it does not yield a digitonide.

The residual alkaline alcoholic extract after evaporation of the alcohol, treatment with water, acidification with dilute sulphuric acid, and extraction with ether, yields a yellowish-brown resin.

The white crystalline extract of madar juice is insoluble in water and non-poisonous to animals, even when injected in oily solutions. The resin also is only slightly toxic to frogs, but the serum is very poisonous, 0·05 ml. killing a frog in a few minutes; the symptoms and post-mortem appearances suggest that it probably acts as a cerebro-spinal poison. The following scheme of examination is now in use in this laboratory in cases of suspected madar juice poisoning:

The alcoholic extract of the suspected material is divided into two portions (*a*) and (*b*)—

(i) Portion (*a*) is saponified with alcoholic potash and extracted with petroleum spirit. The extract is evaporated to dryness, the residue is taken up with a little chloroform, treated with a slight excess of a solution of digitonin in rectified spirit and evaporated again to dryness, and the new residue is extracted with ether. This ethereal solution when evaporated gives a crystalline residue if madar juice was present. A little of the solution, treated with conc. sulphuric acid on a porcelain plate, gives a red colour, which changes to purple on the addition of a few drops of chloroform and of acetic anhydride. The test may also be carried out on a watch-glass placed over a porcelain slab.

The alkaline alcoholic solution, after extraction with petroleum spirit, is evaporated nearly to dryness, taken up with absolute alcohol, and filtered. The filtrate, when treated with excess of hydrogen chloride gas and allowed to stand for some time, has, on dilution with warm water, a characteristic pleasant ester odour, if madar juice was present.

(ii) The other portion (*b*) is evaporated to dryness, the residue is taken up with water acidulated with acetic acid, and the solution is filtered, treated with excess of lead acetate and again filtered. The filtrate is treated with excess of hydrogen sulphide, filtered free from lead, and evaporated to dryness on the water-bath. The residue is extracted with absolute alcohol, and the alcoholic solution is evaporated to dryness. A little of this extract, on injection into a frog, produces, in the presence of madar juice, convulsions ending in paralysis and death, with a bloated appearance. (*Cf.* ANALYST, 1931, **56**, 665; 1932, **57**, 717; 1934, **59**, 542; 1935, **60**, 759; 1936, **61**, 613; also Chatterji, ANALYST, 1930, **55**, 683.)

CROTON POISONING.—A man and his brother were suspected of having stolen two bales of yarn and Rs.200 from their co-tenant. The villagers enlisted the services of a quack, who, having called them before an idol, told them that the wrath of the god would be visited on the guilty person. He then distributed pills to each of the assembled villagers, giving white pills to the two suspected brothers and black pills to the others. One brother swallowed the whole pill, but the other, more cautious, ate only a part of his pill. The first victim suffered from purging, vomited blood and died within 24 hours. His brother was treated by a doctor and recovered. The doctor, suspecting poisoning, informed the police, who secured the uneaten portion of the pill. The viscera of the dead man were found to contain tissue similar to that of the outer covering of croton seeds. The same tissue was also found in the portion of the pill and on a grinding-stone. The quack was arrested, tried, and sentenced to two years' rigorous imprisonment.

Poisoning by Bamboo Shoots.—The juice of crushed tender bamboo shoots was given to a woman as an abortifacient. She suffered from vomiting and purging and died in about 4 hours. Post-mortem examination showed a discharge of froth from the mouth and nose. The heart was full of dark liquid blood and the pericardium contained serous fluid. The lungs, throat, peritoneum, and inner surface of the stomach and intestines were congested, and there were spots of haemorrhage in the mucous membrane of the stomach.

The viscera yielded a non-alkaloidal poisonous extract which agreed in chemical and physiological reactions with the extract obtained from tender bamboo shoots.

The poisonous principles were extracted as follows:—The acid alcoholic extract, after evaporation of the alcohol, was extracted with water, and the aqueous filtrate was treated with lead acetate to remove tannins. The excess of lead in the filtrate was removed by the addition of sodium phosphate and filtration. The filtrate, on extraction with ether, yielded a white crystalline residue freely soluble in water. This residue was found to be poisonous to frogs, producing strychnine-like convulsions. It had no action when painted directly on the exposed heart of a pithed frog. It did not reduce Fehling's solution. With conc. sulphuric acid it gave a pink colour which, on addition of a few particles of manganese dioxide, gave a purple colour similar to that given by strychnine but of a lighter tint. Ferric chloride yielded a faint purplish colour destroyed by acetic acid

Examination of Dust and Dirt.—The apparatus used in this laboratory for collecting loose dirt or dust from the clothing, etc., is a tube, drawn out to a sealed capillary at its lower end, and containing a mixture of alcohol and glycerin, through which the dust can be drawn by means of a wash-bottle type of fitting. After collection of the dust, a mixture of ether and alcohol is added, and the tube is enclosed in a centrifuge tube and centrifuged so that the dust is driven into the capillary. The capillary is then snapped off, the sealed tip is broken, and the collected dust is blown out on to a watch-glass, any adherent dust being released by alternate additions of alcohol and water through a fine capillary tube.

A portion of the dust is examined microscopically. Another portion, and also the residue from the evaporated alcohol-ether, is ashed and tested for metals.

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1936

The Department (under the direction of Mr. M. Jamieson) has two branches: the main one (comprising four chemical laboratories and one bacteriological laboratory) in Singapore and a smaller one (a single laboratory) in Penang.

The major portion of the routine work is submitted by the Excise Department and is concerned generally with revenue assessment and control in connection with Liquors, Chandu and Petroleum Revenue Ordinances and with Textile and Rubber Control. The Police Department contributes a large and increasing number of exhibits associated with criminal investigation. From the Medical Department are received materials for toxicological and clinical analyses, well-waters, drugs and medicines. The only samples of food submitted were 3 tins of condensed milk.

Toxicological.—Of 78 exhibits examined at Singapore, 32 contained poisons or substances taken as such. . These included caustic soda (22), crude disinfectant (3), lysol (2) and sodium carbonate, arsenic, alum, chandu and tuba root (1 of each). In 29 specimens examined at Penang poisons or substances taken as such were found in 12, as follows: Caustic soda (7), opium (2), alcohol, prussic acid, clove and cinnamon oil, formic acid, veronal, lysol, citric acid and phenol (1 of each).

Sea Water in Clothing.—In a criminal case the question whether a pair of trousers had been in sea water was of significance. Tests for traces of bromide were successfully used to establish the fact (*cf.* Seaber, Analyst, 1936, **61**, 14).

Form of Stains on Clothing.—In another case the form of the staining, produced on trousers by contact with the silencer of a car, showed the direction in which the car was moving relative to the wearer of the trousers. The question whether the car was going forward or was reversing was a salient point in sifting the conflicting evidence in this case—a motor-car accident.

Bleached Writing on Bank Notes.—In a case of receiving stolen notes, four Dutch Bank Notes were examined to establish whether ink-written bank endorsements had been bleached out with a given eradicator (sodium hypochlorite and hydrochloric acid). Experiment disclosed identical effects on the note colour-dyes. Ultra-violet illumination revealed the endorsements, and a fairly satisfactory photographic record was obtained, even without any special filters and although the apparatus available afforded only moderate, oblique illumination.

Time of Alteration shown by Ink.—In a promissory note case, a figure alteration from "20" into "60" was stated by the moneylender to have been made in the presence of the borrower, immediately after it had been written in error. No "flowing" at the stroke crossings was shown under the microscope. Experiments made on the back of the actual note showed that "flowing" occurred up to at least 2½ hours after writing.

Lead in Block Tin Distillery Pipes.—In connection with the investigation of the source of lead contamination in local distillery products 5 samples of block tin, an aluminium plate, and 5 pieces of piping were analysed for lead. In one second-grade sample of block tin 3·25 per cent. of lead was found, and in one poor grade sample no less than 12·7 per cent. of lead.

British Standards Institution

BRITISH STANDARD SPECIFICATION FOR JOINERS' GLUE

(Cake or Powder, Jelly or Liquid, and Casein Glue)

This Specification (No. 745—1937) applies to Glues for Joinery Purposes.

Cake or Powder Glue.—Methods are given in the Appendices for determing the water, chlorides and reaction. The total amount of moisture shall not exceed 18 per cent., and the chloride content shall not exceed 2 per cent. (as NaCl). The *p*H shall not exceed the limits 5·0 and 8·5. The joint strength in shear (*i.e.* the load required to break the specified glued joint) shall not be less than 1000 lb. when determined by the method described. The glue shall keep for at least 12 months when stored in a cool dry place.

Liquid Glue.—The reaction shall be not less than *p*H 4 or higher than *p*H 8, and the joint strength in shear not less than 1000 lb. The keeping qualities should be the subject of agreement between purchaser and vendor.

Casein Glue.—The material shall be in the form of powder, and its joint strength in shear shall be not less than 1000 lb. It shall show no signs of decomposition after storage for 12 months in air-tight containers in a cool place.

Copies may be obtained from the British Standards Institution, Publications Department, 28, Victoria Street, London, S.W.1. Price 2s. net, post free 2s. 2d.

BRITISH STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COKE AND COAL

This British Standard (No. 735—1937) is not intended to replace B.S.S. No. 420—1931 or B.S.S. No. 496—1933, which were prepared to meet the requirements of buying and selling of coal and coke. Rather is it an extension, with special provision for the greater accuracy called for in plant performance tests.

The Specification is in three parts:—

I. SAMPLING.—(1) Introduction. (2) Collection of gross sample. (3) Weight of gross sample. (4) Reduction of gross sample (A, samples for moisture; B, samples for analysis). (5) Sampling for shutter test for coke. (6) Containers for samples.

II. ANALYSIS OF COAL SAMPLE.—(1) Determination of moisture (A in "moisture sample," B in air-dried "analysis sample"). (2) Volatile matter. (3) Ash. (4) Calorific value. (5) Other methods. (6) Method of reporting analysis of coal.

III. ANALYSIS OF COKE SAMPLE.—(1) Determination of total moisture. (2) Preparation of sample for analysis. (3) Moisture in air-dried "analysis sample." (4) Volatile matter. (5) Thermal value of volatile matter. (6) Ash. (7) Calorific value. (8) Other methods. (9) Shutter test. (10) Bulk density. (11) True specific gravity. (12) Apparent specific gravity. (13) Trommel test. (14) Method of reporting physical tests and analysis of coke.

APPENDICES.—A, Dimensions of British Standard Test Sieves. B, Summary of experimental evidence *re* collection of moisture sample. C, Suitable forms of sample dividends.

Copies may be obtained from the British Standards Institution, Publications Department, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net, post free 3s. 9d.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Estimation of the Degree of Putrefaction of Meat, Fish and Fat. R. Strohecker, R. Vaubel and H. Kirchberg. (*Z. anal. Chem.*, 1937, **110**, 1–11.)—Earlier methods for the detection of putrefaction in meat and fish are considered unsatisfactory because various types of bacteria produce widely different results. As volatile, strong-smelling compounds are formed during the putrefaction of meat, fish and fats, it is proposed to measure the degree of putrefaction by distilling off these products with steam and examining the distillate. For meat, 10 g. of the minced sample are mixed with 10 g. of water and allowed to stand for 30 minutes in a 100-ml. distillation flask, 5 ml. of dialysed ferric hydroxide solution are added to prevent frothing, and steam-distillation is continued until 30 ml. of distillate have been collected. With fish, addition of ferric hydroxide does not prevent frothing, and tannic acid solution must be used. Ten g. of fish are cut up with a knife, treated with 20 ml. of 1·2 per cent. tannic acid solution, and allowed to stand for 30 minutes in the distillation flask, and 30 ml. are steam-distilled as with meat. Fat (10 g.) is steam-distilled directly, without any addition. The distillation flask is heated with a small flame if the material tested is meat or fish, but must not be heated when fat is examined. The volatile products may be estimated by titration with acid permanganate solution (*cf.* Issoglio, *Giorn. Farm. Chim.*, 1916, **65**, 241, 281, 321; *Annali. Chim. Applic.*, 1916, **6**, 1; Abst., ANALYST, 1916, **41**, 304). Ten or 20 ml. (as required) of *N*/10 potassium permanganate solution are added to 30 ml. of distillate, and the solution is boiled gently for 10 minutes, and then decolorised with 10 ml. of *N*/10 oxalic acid solution, the excess of which is titrated with permanganate solution. The standard potassium permanganate solution contains 40 ml. of conc. sulphuric acid per litre. Before use, it is refluxed for 30 minutes, cooled, and filtered through asbestos. Owing to decomposition during this process, an $N/10$ solution requires 4·4 g. of potassium permanganate per litre (an $N/100$ solution only 0·35 g. per litre). The "oxidation number" for meat is the number of ml. of $N/10$ permanganate required for 100 g. of dry fat-free material. For fish or fat it is calculated on the dry material. The volatile products from fats may also be estimated by the chlorine number, *i.e.* the number of ml. of $N/10$ sodium thiosulphate solution required for 100 g. of dry fat when treated as follows:—The distillate (30 ml.) is mixed with 20 ml. of approximately $N/100$ sodium hypochlorite solution, heated on a boiling water-bath for 15 minutes, and cooled for two minutes under the tap. Ten ml. of 10 per cent. freshly-prepared potassium iodide solution and 5 ml. of 25 per cent. hydrochloric acid are added and, after standing in the dark for 2 minutes, the solution is titrated with $N/100$ thiosulphate solution. A blank test is made, and the difference between the two results gives the chlorine number. The chlorine numbers for fresh fat are somewhat higher than the oxidation numbers, whilst for rancid fats they are lower. (For the oxidation numbers of fats $N/100$ solutions must be used, and the factor for the permanganate must lie between 0·8 and 1·2. The calculation is as above.) The oxidation number is preferable to the chlorine number for meat and fish. Samples of meat (beef, pork, and veal), fish (cod, salmon and haddock), and many fats were examined after being kept for various times. The *p*H was also determined, and the freshness as indicated by appearance, smell, and (for fats) taste were noted. Typical results were:

	Oxidation number	*p*H
Beef, fresh	<20	6·16–6·20
,, putrefying ..	>30	$>6·3$
Fish, fresh	33–50	6·68–7·34
,, putrefying ..	>60	$>7·5$

For fresh fats, chlorine values of 3·2 to 5·4 were obtained, and for the corresponding rancid fats they were from 4 to 20 times as great. Tests for aldehydes and ketones in the distillates do not afford reliable indications of incipient putrefaction, but only show advanced decomposition. E. B. D.

Presence of Octadecatrienoic Acids in Seed-Oils of Pomegranate, Karasu-Uri (*Trichosanthes cucumeroides*) and Balsam Pear. Y. Toyama and K. Uozaki. (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 249–250B.)—An extract of crushed pomegranate seeds in petroleum spirit was filtered and evaporated, and the residual oil had the following values:—n_D^{20}, 1·5174; Wijs iodine value (reaction time, 2 hours, and excess of reagent, 68·9 per cent.), 155·8; maleic value (see Ellis and Jones, ANALYST, 1936, **61**, 812), 20·9. A solution in alcohol of the fatty acids derived from the oil was then neutralised with an alcoholic solution of potassium hydroxide and treated with a solution of magnesium acetate in 90 per cent. alcohol. Punicic acid (m.p., 43·5° to 44° C.; maleic value, 38·6 to 40·7) was separated from the fatty acids in the filtrate after removal of the magnesium salts and purification by re-crystallisation twice from 80 per cent. alcohol; this confirms the earlier work of Toyama and Tsuchiya (ANALYST, 1935, **60**, 570) and of Farmer and Heubel (*J. Chem. Soc.*, 1936, 1809). The corresponding oil from karasu-uri seeds had the following values:—n_D^{20}, 1·4961; iodine value (excess of reagent, 68·6 per cent., *cf. supra*), 138·0; maleic value, 14·6. Treatment as described above yielded a saturated acid (m.p., 64·0° to 64·5° C.; iodine value, 1·49), but trichosanic acid, which was found in a previous experiment (see ANALYST, **1936**, **61**, 703), could not be detected. The liquid fatty acid obtained from the filtrate after removal of the saturated acid was dissolved in petroleum spirit and iodine was added, and on the next day crystals had deposited which were purified (m.p. 69·5° to 70° C.) and found to be β-elaeostearic acid; the presence in the fatty acids of a stereo-isomer of this acid was suspected. The oil from balsam pear seeds had the following values:—n_D^{20}, 1·5052; iodine value (excess of reagent, 69·0 per cent.), 131·4; maleic value, 55·0. The acid isolated in the usual way (*cf. supra*) had m.p. 45·5° to 46·0° C., and, although no change in m.p. occurred when it was mixed with various proportions of α-elaeostearic acid (m.p. 47·5° to 48·0° C.) prepared from wood oil, addition of 10 per cent. of punicic acid or of a mixture of stearic and palmitic acids lowered the m.p. The maleic value was 78·2, the calculated value for α-elaeostearic acid being 91·2, and treatment with iodine yielded β-elaeostearic acid. Trichosanic acid could not be detected (*cf. supra*), and the conclusion was drawn that the acid was impure α-elaeostearic acid. The results obtained with karasu-uri and balsam pear seed oils are at variance with those previously recorded (*loc. cit.*), trichosanic acid being then found, and it is considered either that this acid was present in a form which crystallises only with difficulty, or that it was converted by isomerisation into α-elaeostearic acid.

J. G.

Oil from the Seeds of *Ximenia Americana* Linn. A New Unsaturated Fatty Acid, Ximenic Acid. S. V. Puntambekar and S. Krishna. (*J. Indian Chem. Soc.*, 1937, 14, 268–274.)—*Ximenia americana*, Nat. Order *Olacaceae* is a shrub found on the Tennasserim coast, the south Mahratta country, Mysore and many parts of the Madras Presidency. The orange-red drupes are used for jam, and the kernels taste like filberts or, when roasted, like almonds. In Southern India the oil is used as a substitute for ghee. The seeds examined consisted of air-dried pulp and shell, 55 per cent., and kernels 45 per cent., containing moisture 3·6 and oil 49 per cent. The extracted pale yellow oil had sp.gr. at 20/15° C., 0·9262; n_D^{20}, 1·4710; saponification value, 169·2; iodine value (Hanus), 82·5; acid value, 2·3; Reichert-Meissl value, *nil*; unsaponifiable matter, 1·7 per cent. The mixed acids had mean molecular equivalent 319·8, and iodine value 85·0, and were separated by Twitchell's method into saturated acids 31, unsaturated acids 67·5, and resin acids 1·5 per cent. The high iodine value of the solid acids (33·9) indicated their association with an unsaturated acid other than oleic acid, and this was confirmed by oxidation with alkaline permanganate. No dihydroxystearic acid was obtained, but an acid which, when twice crystallised from 95 per cent. alcohol, had m.p. 118°–119° C., molecular equivalent 425, and an elementary composition agreeing with that of a dihydroxy derivative of an unsaturated solid acid, of 26 C atoms, accompanying cerotic acid, which was the main constituent of the solid acids. Catalytic hydrogenation of the crystallised solid acids (m.p. 61°–62° C., molecular equivalent 400·5, iodine value 43·7) from the 4th fraction of the distilled esters of the solid fatty acids supplied additional proof. The product had m.p. 83°–84° C., molecular equivalent 398·4, and iodine value *nil*, and was identified as cerotic acid. The acid has not yet been separated in a pure state owing to its intimate association with cerotic acid, but it has been named ximenic acid. Part of the liquid acids was saponified and oxidised with potassium permanganate, and part was converted into the methyl esters and fractionally distilled. From the results the fatty acids were calculated to have the following composition:—stearic (not isolated in the pure form), 1·2; cerotic, 15·2; ximenic, 14·6; oleic, 60·8; linolic, 6·7; resin acids, 1·5 per cent. D. G. H.

Alkaloids of *Lupinus laxus* Rydb. J. F. Couch. (*J. Amer. Chem. Soc.*, 1937, **59**, 1469–71.)—Two lots of *Lupinus laxus*, a species closely related to *L. laxiflorus*, were collected at Fish Lake, Utah, in 1932 and in 1934. The first lot, collected in August, consisted of the entire above-ground parts of the plant in flower. The second lot, collected in July and August, consisted of similar plants in all stages of maturity. The dried plants were ground to a coarse powder, and extracted with alcohol, and the alkaloids were recovered from the extract (*cf.* Couch, *J. Amer. Chem. Soc.*, 1934, **56**, 2434). Four alkaloids were isolated—sparteine, *d*-lupanine, trilupine and a minute quantity of an alkaloid isomeric with hydroxylupanine. A preliminary separation was made by fractional distillation under reduced pressure. From one fraction (b.p. 150° to 175° C. at 5 mm.), sparteine was precipitated as disulphate from acetone; *d*-lupanine was obtained as the dihydrochloride from a second fraction (b.p. 200°–250° C. at 6 mm.), similarly dissolved, and trilupine was recovered from the residual acetone after the crystallisation of *d*-lupanine dihydrochloride. The fourth substance, obtained from a fraction of b.p. 220°–245° C. at 3 mm., was insoluble in acetone; it is only provisionally accepted as a new alkaloid pending the examination of further material. The other alkaloids were identified by comparison of their physical properties and those of their salts with those of the corresponding authenticated bases and salts. No depression of the melting-points occurred when corresponding salts were mixed. The yields of total alkaloid (calculated on the dried plants) were (i) 2·19 per cent.; (ii) 2·93 per cent. Full particulars of methods of separating the alkaloids are given. E. B. D.

Isolation of Erythroidine from *Erythrina Americana* Mill. K. Folkers and R. T. Major. (*J. Amer. Chem. Soc.*, 1937, 59, 1580–1581.)—Extracts of the seeds of *Erythrina americana* Mill., which resemble curare in their physiological effect (*cf.* Altamirano, *Gaceta Medica de Mexico*, 1888, **23**, 369; *J. Pharmacol.*, 1937, **60**, 71), have been proposed as a substitute for that drug in pharmaceutical preparations for use against tetanus. A pure crystalline alkaloid, erythroidine, which causes the curare-like motor paralysis, has now been isolated from the bases present in the seeds. The toxicity of erythroidine hydrochloride was determined on white mice by Trevan's method, and results are given for oral and subcutaneous administration. A modified Claude Bernard test of the curare action on frogs showed that injection of 0·1 to 0·15 mg. per frog into the lymph sac caused complete motor paralysis. Unlike curare, erythroidine is effective when administered orally. The yield of erythroidine was 0·7 to 0·9 per cent. of the seed weight. It was soluble in water, benzene, chloroform, methanol and alcohol, and moderately soluble in ether; empirical formula, $C_{16}H_{19}NO_3$; m.p., 94°–96° C. The hydrochloride crystallises in needles, $C_{16}H_{19}NO_3.HCl$, melting with decomposition at 228°–229° C.; $[\alpha]_D^{31}$, +109·7°. E. B. D.

Determination of the Alkaloids of Opium and their Derivatives by the Mercurimetric Method. A. Ionescu-Matiu and C. Ichim. (*J. Pharm. Chim.*, **1937**, **26**, 49–56.)—The mercurimetric determination of organic compounds (*J. Pharm. Chim.*, 1926, **4**, 533; Abst., ANALYST, 1927, **52**, 100) consists in the precipitation of the compounds by mercuric salts and subsequent determination of the mercury. For opium alkaloids and their derivatives, excess of the Mayer-Walzer reagent (10 g. of potassium iodide to 15 g. of mercuric iodide in water) is added to a known weight of the substance to be tested, from 5 to 10 ml. of the reagent being used for 1 to 3 mg. of the sample. The resulting precipitate is centrifuged, washed several times with water acidified with 10 per cent. sulphuric acid, dissolved in 10 to 15 ml. of a mixture of sulphuric and nitric acids (strengths not given) and transferred to an Erlenmeyer flask. The solution is boiled to transform the mercury completely into mercuric sulphate, diluted with water to 100 ml. and, after destruction of nitrous compounds by adding a few drops of 2 per cent. potassium permanganate solution until a pink colour is obtained, the mercury is precipitated with 10 to 12 drops of 10 per cent. sodium nitroprusside solution. The turbid liquid is then titrated with *N*/10 sodium chloride solution until it becomes clear, a micro-burette being used. The method gives satisfactory results with apomorphine, heroin, dionine, narceine and pantopon. By comparative determinations with the silicotungstate and other methods the following equivalents were established:

1 ml. of *N*/10 sodium chloride solution = 0·0263 g. of apomorphine
1 ml. ,, ,, ,, ,, ,, = 0·0204 g. of anhydrous heroin
1 ml. ,, ,, ,, ,, ,, = 0·0294 g. of dionine ($2H_2O$)
1 ml. ,, ,, ,, ,, ,, = 0·025 g. of narceine
1 ml. ,, ,, ,, ,, ,, = 0·021 g. of pantopon (total alkaloids as hydrochlorides)

E. B. D.

Histology of Indian Podophyllum. T. E. Wallis and S. Goldberg. (*Pharm. J.*, 1937, **139**, 103.)—Indian podophyllum consists of the rhizome and roots of *Podophyllum Emodi* Wall, and the commercial drug contains about 75 per cent. of the roots. The rhizome differs from that of the American drug in the very small development of the internodes, and therefore consists of structures which resemble the enlarged, rather than the elongated, portions of the rhizome of *P. peltatum*. The surface of the rhizome is covered with cork which is composed of thin-walled, polyhedral, isodiametric cells, which resemble the cork found in small amount on the leaf-scars of the enlarged portions of American podophyllum. The elongated, rectangular, brown epidermal cells, which are so characteristic of the long internodes of *P. peltatum*, are absent, and this feature forms a very useful point of distinction. The transverse section of the Indian rhizome shows a circle of nine to eighteen vascular bundles, which are somewhat radially elongated and are separated by fairly broad medullary rays. The pith in the centre occupies about one-third of the total diameter of the rhizome (in *P. peltatum* the pith occupies about one-half of the total diameter of the cylindrical portions). The pith and the cortex contain many starch granules, sometimes simple but more frequently compound, having from two to twenty components. The individual granules, which measure from 2 to 34μ (average 7μ), are rather smaller than those of the American drug. Calcium oxalate crystals are present in some of the cells as cluster crystals measuring from 20μ to 60μ (average 30μ); those of *P. peltatum* frequently exceed 60μ. Pericyclic fibres are absent, except in the more cylindrical portions of the rhizome, where a small number may be found. In the pith, near the inner margin of the primary xylem, are small groups of sclerenchymatous cells, which are irregular and contorted and rarely exceed 500μ in length; similar cells in American podophyllum have a maximum length of 1 mm. The roots have a structure similar to those of the American drug, except that cluster crystals of calcium oxalate are completely absent. For the histology of American podophyllum see Wallis and Goldberg (*Pharm. J.*, 1937, **10**, 40; Abst., ANALYST, 1937, **62**, 564). S. G. S.

Composition of Pyrasulf. M. J. Schulte. (*Pharm. Weekblad*, 1937, **74**, 1081–1086.)—Pyrasulf has been stated to be a molecular compound of 2 mols. of pyramidone and one of strontium sulphosalicylate, $(C_{13}H_{17}N_3O)_2$, $C_7O_6H_4SrS$. It is used as an antipyretic and antineuralgic, and its effect is claimed to be greater than that of a mixture of its components, owing to its solubility in water and the ease with which it is absorbed by the system; it can also be administered in large doses. It is sometimes used in conjunction with other substances, *e.g.* "Verasulf" and "Pavyco" are combinations of pyrasulf with somnacetin or with a mixture of papaverine hydrochloride and eumydrinum (known as "papavydrin"), respectively. It is pale yellow, has a bitter taste, and at room temperature dissolves slowly in water (solubility, 1 in 10); warm conc. solutions deposit crystals having the properties of pyramidone. In alcohol, however, only 60 per cent. of it dissolves, the soluble portion having the properties of pyramidone, and the residue those of strontium sulphosalicylate. A quantitative separation made in this way indicates that the 2 mols. of water of crystallisation associated with the strontium salt are retained in pyrasulf. When heated, pyrasulf becomes an opaque mass at 104° to 106° C., but does not melt completely, and since the m.p. of pyramidone is 106° to 107° C. and strontium sulphosalicylate has no defined m.p., the observed m.p. is to be regarded as that of impure pyramidone. Analyses of mixtures of the two constituents confirm the conclusion that pyrasulf has the composition

$$2(C_{13}H_{17}N_3O),\ C_6H_3OH(SO_3)(COO)Sr,\ 2H_2O.$$

It is prepared by melting the two constituents together. The m.p. of pyramidone is below the temperature (120° C.) at which strontium sulphosalicylate loses its water of crystallisation; the solubility of pyramidone is unaffected by the presence of the sulphosalicylate. It therefore seems unlikely that pyrasulf has a greater therapeutic effect than that of a simple mixture of its constituents, as the only difference is that in the former one of the constituents has undergone slight decomposition. J. G.

Adsorption Fluorescence Reaction of Various Species of Rhubarb. S. K. Crews. (*Pharm. J.*, 1937, **139**, 114.)—The adsorption fluorescence test previously described (*Pharm. J.*, 1936, **136**, 720; Abst., ANALYST, 1936, **61**, 558) has been used to test other samples of rhubarb; the Wasicky borax fluorescence test (*Fluorescenzerscheinungen*, 1924) has also been used. The results are indicated in the following table.

No.	Kind	Species	Source	Fluorescence of drug	Fluorescence adsorption test	Fluorescence of solution	Wasicky borax test
1	Siberian	*R. palmatum* L.	D. Hanbury, 1874	Brown, blue in centre	Intense	Bright blue	Bright blue
2	Russian	—	A. S. Hill & Son	Light brown, blue in centre	Negative	Pale maroon	Maroon
3	Banbury	*R. macropterum* Mart.	R. Usher	Brown, no blue	Intense	Pale violet	Bright blue
4	India	*R. emodi* Wall.	Dr. Royle	Brown, no blue	Intense	Blue	Bright blue
5	182, 1886 Nepa	*R. emodi* Wall.	Col. & Ind. Exhib.	Brown, no blue	Negative	Red brown	Golden brown
6	Canton stick	—	Dr. Dymock	Brown, no blue	Sl. positive	Orange	Golden brown
7	China, 1890	*R. officinale* Baill.	Professor Henry	Brown	Negative	Dull green	Pale green
8	Turkestan	*R. tartaricum* L. fil.	Dr. Regel	Brown and blue	Negative	Very dull blue	Pale blue
9	—	"*R. alpinum*"	R. Usher	Brown	Faintly positive	Luminous yellow	Dull blue
10	Himalaya	*R. nobile* Hook, J. and Thoms	Sir J. D. Hooker	Dark brown and blue	Intense v.f. positive	Dull blue	Pale blue
11	Scinde	*R. ribes* L.	J. E. Stocks	Brown, some blue	—	Slate	Pale blue
12	Kashmir	*R. ribes* L.	Aitchison, 1878	Brown, bright blue	Positive	Blue	Bright blue
13	Bengal	*R. emodi* Wall.	Col. & Ind. Exhib.	Light brown, no blue	Negative	Golden brown	Golden brown
14	Austrian	Medicinal	Jenkins & Phillips	Mauve	Intense	Violet	Bright blue
15	India	*R. moorcroftanium* Royle	179, 1883 Amsterdam Exhib.	Light brown	Negative	Brown	Golden brown
16	Banbury	*R. officinale* Baill.	48, 1888 Usher	Brown	Negative	Dull brown	Dull green
17	Banbury	*R. rhaponticum*	R. Usher	Dull mauve	Intense	Violet	Violet
18	English	Unknown	—	Dull brown	Intense	Slate	Blue-violet
19	English (sold as Chinese)	Unknown	T. 62, 1907 Crosbie & Co.	Brownish	Negative	Brown	Brown
20	English	English rhubarb	Not stated	Brown, bright blue	Intense	Violet	Blue-violet
21	Indian	*R. emodi* Wall.	United Prov. India	Golden brown	Negative	Red-brown, golden brown	Red-brown
22	Afghanistan	*R. emodi* Wall.	Aitchison 75, 1894	Dull violet	Positive	Violet	Blue
	English	*Rumex* fresh	—	Blue in cambium ring region	Negative	Blue	Blue
	English	*Rumex* dried	1937		Negative	Blue	Green
23	E. Tribet	*R. australe* Don	Dr. Pierre, 111, 1888	Brown	Negative	Brown	Golden brown

As was to be expected, certain specimens had characteristics intermediate between the ordinary Chinese and the rhapontic varieties. S. G. S.

Biochemical

Action of Meat Extracts and Related Substances as Gastric Stimulants in Man. W. R. Boon. (*Brit. Med. J.*, 1937, 412–413.)—Meat extracts have been found to have a stimulant action on the gastric mucosa, and it has also been found that the water-soluble fraction of meat is almost as efficient in stimulating the flow of hydrochloric acid as whole meat. The secretion of hydrochloric acid was greater when a liquid commercial beef extract was used, than even when whole meat was employed. The flow of pepsin was stimulated only when whole meat in the form of beef powder was used. Sodium glutamate had little or no stimulant action, and the stomach emptied rapidly when this substance was used. The stomach emptied least rapidly with whole meat and much more rapidly with beef extracts. S. G. S.

Colour Reaction applied to Liver Extracts. G. E. Shaw. (*Pharm. J.*, 1937, **139**, 115–116.)—The Folin-Marenzi reagent (*J. Biol. Chem.*, 1929, **83**, 109; *cf.* ANALYST, 1929, **54**, 553) and the more distinctive modification of Folin's reagent (*J. Biol. Chem.*, 1933, **111**, 101) have been used to estimate in liver extracts the purine previously described by Jacobson and others (*N. Eng. J. Med.*, 1935, **66**, 212). A number of animal tissues were examined, but, with the exception of rabbit kidney, the colour-reacting substance or chromogen-content was much lower than in bovine liver. It was found that a portion of the chromogenic material in normal bovine liver was precipitated by lead acetate solution and that the presence of small amounts of lead acetate did not interefere with the test. It was also found that an extract from the liver in an untreated case of pernicious anaemia differed both from normal bovine liver extract and from an extract of liver in a treated case of pernicious anaemia. The second two gave a considerable amount of lead-precipitable chromogen, but there was very little of such chromogen in the pernicious anaemia liver. In the untreated case the total colour produced from an extract made as soon as possible from the specimen, which had been frozen, immediately after its removal from the body, gave higher values after varying periods of storage under ether at 4° C. There was, however, no significant change in the amount of lead-precipitable chromogen. This increase in colour was not found with other livers. When the untreated pernicious anaemia liver extract was treated with lead acetate, it gave a cloudy solution which would not settle, even after several days; this was in marked contrast to normal bovine liver extracts and to an extract from the liver in a treated case of pernicious anaemia. The two latter gave flocculent precipitates which settled rapidly. The tests were made by adding 5 ml. of urea cyanide to 0·5 ml. of Extractum Hepatis Liquidum B.P. After shaking, 2 ml. of Folin's uric acid reagent was added, and after 30 minutes the mixture was diluted to 100 ml. with water, and examined in a 1-cm. cell in a Lovibond tintometer. The tintometer reading, multiplied by 200, gave the total chromogen (A) in blue units per ml. The chromogen not precipitated by lead acetate was determined by adding 5 ml. of distilled water to 1 ml. of Extractum Hepatis Liquidum B.P., shaking well, and then adding 1 ml. of 10 per cent. lead acetate solution. The mixture was allowed to stand for 15 minutes and then filtered, and 3·5 ml. were taken for the test. Five ml. of urea cyanide reagent and 2 ml. of uric acid reagent were added as before, and the mixture was diluted to 100 ml. for tintometer examination. The tintometer reading, multiplied by 200, gave the chromogen not precipitated by lead acetate (B) in blue units per ml. With B.P. liquid extracts of liver, values for (A) varied from 220 to 1540, and for (B) from 120 to 1100 units. Proprietary liver extracts for oral administration gave values for (A) from 160 to 4620 and for (B) from 120 to 3020 units. Liver extracts for parenteral administration varied for (A) from 50 to 2620, and for (B) from 46 to 2100 units. Acetone-dried baker's yeast gave 272 units per g., autolysed yeast 4050 units per g., and wheat-germ extract (1 ml. ≡ 5 g.) 872 units per ml. No relationship was found between the colour values of liver extracts and the amount of liver which they were stated to contain. The author suggests that canine black tongue and pellagra are characterised by spinal cord degeneration, and that this is a syndrome, also associated with pernicious anaemia, about which

there have been conflicting reports as to the efficacy of liver extracts. Canine black tongue is specifically cured by a liver purine, and pellagra is very similar to that disease. It is possible that the liver extracts that will cure cord degeneration are rich in purine or chromogen, and those that will not are poor in this factor. Some parenteral liver extracts, which are extremely potent for the remission of pernicious anaemia, are highly purified and have very little chromogen activity.
S. G. S.

New Sources of Urease for the Determination of Urea. M. Damodaran and P. M. Sivaramakrishman. (*Biochem. J.*, 1937, **31**, 1041–1046.)—The seed of the water-melon (*Citrullus vulgaris*) has been found to be a good source of urease suitable for use in urea determinations. The urease from this new source was superior to that obtained from soya bean and jack bean, because with it quantitative results were obtained for urea in materials, such as whole blood and liver, which gave abnormally high values with the urease from the other sources. When soya-bean or jack-bean urease was used with ox-blood and liver it was found that, even under standard conditions, abnormal values were obtained, and that if the time of action or the enzyme concentration were increased, the errors were also increased. Such effects were negligible when water-melon seeds were used.
S. G. S.

Bacteriological

Filter for Bacteria for Use in Biological Work. C. Englehard. (*Z. ges. Brau.*, 1937, **60**, 45–46; *J. Inst. Brew.*, 1937, **43**, 313.)—Glass filters with a special filter-plate (made by Schott u. Gen., Jena) are preferable to the sintered glass, porcelain, Gooch and Allihn types used with laboratory water-pumps. Tests on two designs are described; these delivered 50 ml. of water in 3·5 minutes and 500 ml. in 27 minutes. The mean widths of the pores were 0·650μ and 0·684μ and the maximum pore widths were 0·76μ and 0·91μ, respectively. Suspensions of yeast in water and beer containing a bacterial haze were used for the tests, and the filtrates, when plated out in nutrient gelatin, gave no colonies on incubation. The cleaning of the filters is effected by immersion in conc. sulphuric acid heated to 80° C. and containing potassium nitrate or a mixture of sodium nitrate and sodium perchlorate; no change in the porosity is thereby produced and there is no loss in weight (or less than 1 mg.). Mixtures of sulphuric acid and potassium dichromate are unsuitable for cleaning, since the reduced salt adheres firmly to the surface of the filter and makes it toxic to micro-organisms, etc. Dry or wet sterilisation may be used, but the filter should be gradually heated and gradually cooled in the steriliser. For retention of bacteria and yeasts, maximum pore sizes of 1·5μ and 1·5 to 2·7μ respectively are permissible, and the rate of filtration may thus be accelerated.
D. R. W.

Epidemiology and Symptomatology of *Staphylococcus* Food Poisoning. A Report on Recent Outbreaks. G. A. Dennison. (*Amer. J. Pub. Health*, 1936, [V], **26**, 1168–75; *Bull. Hyg.*, 1937, **12**, 369.)—The main outbreak recorded was traced to cream puffs from one bakery in which the conditions of production were extremely bad in almost every respect. The cream filling of only one batch was involved; this was supposed to be heated in steam. Bacteriological examination of 19 puffs showed in some as many as 50 to 90 bacteria per gram, 90 per cent. being *Staphylococcus aureus*. Nineteen strains were isolated and all were haemolytic. Sterile filtrates of both cultures were administered orally to human volunteers; most of them were mildly ill, one was very ill for 3 hours, and few were unaffected. This outbreak, occurring in March, 1936, chiefly affected high-school students. There were 102 cases in all, and 20 cases unconnected with the school which were traced to cream puffs from the same bakery. The incubation period was mostly 2 to 4 hours; in a few cases 6 to 8 hours. At a later date, in May, after the bakery had been cleaned, there was a second small outbreak (3 cases). All had eaten coconut custard pie made in this bakery. Portions of two of the pies were found to contain enormous numbers of *Staphylococcus aureus*. The three people affected were severely ill and had to be taken to hospital. D. R. W.

Identity of "*Bacterium* X" (Brown) and "*Bacterium* C" (Chapman). J. L. Shimwell and W. F. Kirkpatrick. (*J. Inst. Brewing*, 1937, **43**, 339–342.)—The first serious attempt to estimate the antiseptic value of hops was that of Brown and Ward (*id.*, 1910, **16**, 641; Abst., ANALYST, 1911, **36**, 65) who used a "lactic acid-producing organism" ("*Bacterium* X"). This was chosen because it grew very rapidly in wort or extracts of malt in cold water, and was very sensitive to the antiseptic power of hops, and, since it was isolated from sour beer, the results obtained could be regarded as being due to an actual beer-disease organism. In connection with the work of Shimwell (*id.*, 1937, **43**, 111) on the antiseptic substances of hops, it became necessary to examine a culture of "*Bacterium* X" (obtained from the Lister Institute), and it was noticed that an abundant white surface-growth had been produced on a broth-agar slope. This indicates that, contrary to the original conclusions of Brown and Clubb (*loc. cit.*, and *id.*, 1913, **19**, 261), it is most unlikely that the organism was a *Lactobacillus* type, and that it certainly could not be *L. Pastorianus*. Further experiments showed that the organisms obtained from cultures in the present Lister collection are spore-forming, and that they are strains of *Bacillus cereus* Frankland, one of the commonest aerobic, spore-forming species prevalent in air and dust, etc. Similar conclusions were reached regarding "*Bacterium* C," isolated by Chaston Chapman, and used by him also for the evaluation of hops (*id.*, 1925, **31**, 13; 1929, **35**, 363; Abst., ANALYST, 1930, **55**, 57), and the respective names *B. cereus* var. *arborescens* and *B. cereus* var. *rubicundus* are suggested. The characteristics of these and *B. cereus* are tabulated in full, and it is shown that, although it is possible to distinguish the strains, the differences shown are, on the whole, those of degree. Only one major difference is recorded, namely, that a salmon-pink to maroon coloured growth was produced on potato by "*Bacterium* C," whilst the other two organisms produced a white to dirty-brown or yellow colour. Since *B. cereus* var. *arborescens* will not grow in hopped or unhopped beer or in hopped wort, and since its growth in unhopped wort is prevented if the *p*H is below 5·0 (*i.e.* a value higher than that of unhopped beer used by Brown), it seems unlikely that it is identical with the original "*Bacterium* X." These and other apparent contradictions arising from the descriptions of the properties of the organisms given by Brown and his co-workers (*loc. cit.*) may be explained by the contamination of the original "*Bacterium* X" with spores of *B. cereus* strain, and gradual displacement of the former by the preferential growth of the latter. A culture derived from the organism used by Walker for the evaluation of hops (*id.*, 1924, **30**, 349; 1926, **32**, 491) was also examined and found to be similar to the *B. cereus* organism, and the published results of I. Stoleru, who was engaged on similar work (*Recherches sur les Propriétés Antiseptiques du Houblon*, Paris, 1924), indicate that he also used a similar organism. There is no evidence, in fact, that "*Bacterium* X" has ever been used for the evaluation of hops since 1913 (Brown and Clubb, *loc. cit.*), an important point because it is less hop-sensitive than *B. cereus*, so that results obtained with it would give an exaggerated idea of the potency of hop antiseptics towards beer bacteria. It is also evident that results obtained with *B. cereus* do not correspond with those produced by a true beer-disease organism (*cf. Allen's Commercial Organic Analysis*, 5th Ed., Vol. VIII, 1930, p. 126). J. G.

Agricultural

Selenium in Plants in Relation to its Occurrence in Soils. J. T. Miller and H. G. Byers. (*J. Agric. Res.*, 1937, **55**, 59–68.)—Observations were made over wide areas in Kansas, Colorado and New Mexico, where seleniferous soils (*e.g.* shaly clay loams) and soils relatively free from selenium (*e.g.* sandy and gritty clay loams) containing 2·0 to 4·0 and 0·2 p.p.m. of selenium, respectively, occur in juxtaposition. The data indicate that plants may be classified roughly into 3 groups according to their tolerance of selenium in the soil, *viz.*:—(1) Plants that absorb selenium readily, *e.g. Astragalus racemosus, A. pectinatus, A. bisculatus, A. carolianus* L., *Stanleya pinnata, S. bipinnata, Applopappus fremonti, Xylorrhiza Parryi* (A. Gray) Greene, and probably other species of the same and different genera. Not all species of a given genus have the same properties in this respect; for example, *Astragalus missouriensis, A. mollissimus* and *A. Drummondii* Dougl. have been found to contain very small quantities of selenium even when growing on a highly seleniferous soil. The highly-selenised plants found on seleniferous soils are usually absent from (or are very rare on) adjacent non-seleniferous areas, and since they are consistently high in selenium (*e.g.* 4,000 p.p.m. in *A. pectinatus*) and yet grow vigorously, it is possible that selenium may be of physiological importance to them; the three *Astragalus* species were, in fact, not observed outside the seleniferous portion of the Kansas district. (2) Plants that can absorb moderate or large quantities of selenium without severe injury, *e.g.* white wreath and blue asters, turpentine weed, sunflower, western wheatgrass (*Agropyron Smithii* Ryab.), wheat, rye, barley and corn. These occur widely distributed on both seleniferous and other areas. The extent of the retardation of the growth of these plants by small quantities of selenium is not known, but it is certain that the limit of tolerance is rather low. (3) Plants that have a very limited tolerance of selenium and are able to absorb only small quantities from seleniferous soils, *e.g.* buffalo grass and the grama grasses (*Bouteloua gracilis* and *B. curtipendula*). When the selenium-content of the surface soil is high these plants are rare and make poor growth or are absent. The recorded selenium-contents of vegetation from non-seleniferous and seleniferous soils in p.p.m. vary, respectively, from 0 (*Bouteloua gracilis*) to 2 (cocklebur, *Xanthium* sp.), and from 1 (scarlet mallow) to 330 (*Stanleya pinnata*), *A. pectinatus* (*cf. supra*) being exceptional. The soils tested had *p*H values of 7·5 to 8·4, and no evidence was obtained that selenium absorption is influenced by the *p*H value (*cf.* Byers and others, *U.S. Dept. Agric. Tech. Bull.*, 1935, 482; 1936, 530; *Ind. Eng. Chem.*, 1935, **27**, 902; 1936, **28**, 912; Abst., ANALYST, 1935, **60**, 774). J. G.

Determination of Lactic Acid in Sour Feeding Stuffs. Flieg. (*Chem.-Ztg.*, 1937, **61**, 601.)—The lactic acid in the residue left after three distillations of sour feeding stuffs by Wiegner's method is oxidised to acetic acid by means of chromsulphuric acid, and the resulting acetic acid is determined in a fourth distillate. This was found to contain, on the average, acetic acid corresponding with 41·09 per cent. of lactic acid and 41·18 per cent. of acetic acid which had been left in the residue from the third distillation (18·13 per cent. of the total acetic acid). The acetic and butyric acids in sour feeding stuffs do not influence the lactic acid value. Volatile materials oxidisable to acetic acid are removed by the preliminary distillations, and the results obtained are affected only by those substances which on oxidation yield acids other than carbon dioxide. Proteins, amino acids and acids containing no oxygen except that in the carboxyl group have no effect. Compounds containing hydroxyl or keto groups, which are oxidised by chromsulphuric acid to acetic acid, are present in sour feeding stuffs in such small quantities that they do not cause errors greater than 0·05 per cent. in the lactic acid figure. E. M. P.

Organic

Addition of Thiocyanic Acid to Olefinic Double Bonds. M. S. Kharasch, E. M. May and F. R. Mayo. (*J. Amer. Chem. Soc.*, 1937, **59**, 1580.)—Isobutylene formed addition compounds with thiocyanic acid when treated with an equimolecular amount in ethereal solution at room temperature for 4 hours. An oil (b.p. 51°–54° C. at 25 mm.) was obtained. This yielded derivatives of *t*-butyl thiocyanate and *t*-butyl isothiocyanate (*e.g.* *t*-butyl-N-acetyldithiocarbamate and *t*-butylthiourea). Quantitative determinations of the thiocyanate and isothiocyanate gave the results:—*t*-butyl thiocyanate, 32 per cent.; *t*-butyl isothiocyanate, 62 per cent.; unknown, 6 per cent. When the reaction mixture of isobutylene and thiocyanic acid was kept at 0° C. an oil (b.p. 53°–54° C. at 25 mm.), which contained 42 per cent. of *t*-butyl thiocyanate, was obtained. Thiocyanic acid also formed similar addition compounds with trimethylethylene, styrene, 2-pentene and camphene. The effect of peroxides and other catalysts on the addition of thiocyanic acid to olefinic double bonds is to be studied. E. B. D.

Analytical Uses of Nessler's Reagent. III. Determination of Formaldehyde, Pyrogallol, Tannin and Gallic Acid. M. Goswami and A. Shaha. (*J. Indian Chem. Soc.*, 1937, **14**, 208–213.)—An alkaline solution of potassium mercuric iodide gives up iodine and liberates mercury in the presence of formaldehyde strictly according to the reaction $CH_2O + K_2HgI_4 \rightarrow Hg + H.COOH$, as with reducing sugars (ANALYST, 1936, **61**, 356). The micro-determination also gave good results, and 1 part of formaldehyde in 100,000 could be determined with a fair degree of accuracy. The method was then used to determine the absolute oxygen value of pyrogallol. In the absence of oxygen it was found that 1 mol. of pyrogallol always liberated 2 atoms of mercury, corresponding with 2 atoms of oxygen. With tannic and gallic acids it was possible to work in an ordinary atmosphere. One mol. of pure tannin (pentadigalloylglucose) absorbed 16 atoms of oxygen, whilst 4 mols. of gallic acid required 11 atoms. Various dilutions were tested, and the method was successfully applied to quantitative determinations. Formaldehyde was determined as follows:—Five ml. of hexamethylenetetramine solution (0·302 g. in 250 ml.) corresponding with 0·0077 g. of formaldehyde were placed in a flask fitted with dropping funnel, trap and a condenser, the end of which was connected with an adapter and fitted to a wide-mouthed bottle containing Nessler's reagent (2·5 g. of mercuric chloride, 8 g. of potassium iodide, 100 ml. of water, and 50 ml. of 30 per cent. sodium hydroxide solution), followed by a second guard-bottle also containing Nessler's reagent. Thirty-five ml. of 15 per cent. sulphuric acid were added to the tetramine solution and the whole was distilled. The mercury was precipitated in the first bottle, the Nessler solutions from the two bottles were mixed and acidified with glacial acetic acid, and standard iodine solution was added. After solution of the liberated mercury the excess of iodine was titrated with standard thiosulphate solution. The absolute oxygen value of pyrogallol was determined in a special apparatus in an atmosphere of coal gas, and minute directions are given for manipulating the various stopcocks to render the apparatus air-free and for introducing the solutions. The following results are typical of those obtained with tannin and re-crystallised gallic acid (0·051 *N* thiosulphate solution and 10 ml. of iodine solution were used):

		Thiosulphate required		Tannin	
Tannin in 250 ml. g.	Vol. added ml.	Before oxidation (A) ml.	After oxidation (B) ml.	Found (A − B) × 0·8053 g.	Present g.
0·3020	10	15·5	11	0·0122	0·0121
1·1919	1	15·5	13·7	0·0049	0·0048
Gallic acid in 250 ml. g.					
0·2775	10	17·2	10·55	0·0113	0·0011
1·2019	1	17·2	14·3	0·0049	0·0048

D. G. H.

Colour Reactions of Aromatic Amines. C. Cândea and E. Macovski. (*Bull. Soc. Chim.*, 1937, 4, 1398–1401.)—Aromatic amines give characteristic colours when treated in dilute acetic acid solution with aqueous ammonium persulphate solution. The colour appears slowly in the cold and more rapidly in the presence of a few drops of silver nitrate solution or on heating; the speed of the reaction increases with the concentration of the silver ions. Suitable quantities are 2 ml. of a solution of the amine in 10 per cent. acetic acid, 1 ml. of 10 per cent. ammonium persulphate solution and 5 drops of 5 per cent. silver nitrate solution;

the acetic acid solution of the amine should be dilute. The amines investigated gave perceptible colours at concentrations down to 0·01 per cent. The following results are given:

Amine	Concentration of amine solution Per Cent.	Colour
Aniline	1	Blue precipitate
,,	0·1	Cherry-red
Monomethylaniline	0·1	Emerald-green
Dimethylaniline	0·1	Yellow
o-Toluidine	0·01–1	Various
Xylidine (*o*-, *p*-)	0·01–1	Pinkish-violet
o-Anisidine	0–1	Red
p-Anisidine	0·01–1	Violet
α-Naphthylamine	0·01–1	,,
Benzidine	0·01–1	Yellow
Dianisidine	0·01–1	Red
Diphenylamine	dilute solutions	Various
Diethylaniline	1–5	Yellow
Tetramethyldiaminodiphenylmethane	0·01–1	Greenish-yellow
,, ,,	greater than 1	Various

E. M. P.

Use of the "Oily Matter" isolated in Determining the "Burton-Robertshaw Index" of Sulphated Oils for the Determination of the Iodine Value. D. Burton and G. F. Robertshaw. (*J. Int. Soc. Leather Trades Chem.*, 1937, **21**, 366–369.)—Owing to the difficulty of determining the iodine value of sulphated oils, the carbon tetrachloride extract obtained in determining the Burton–Robertshaw index (ANALYST, 1937, **62**, 64) has been used for the determination of the iodine value by the Rosenmund and Kuhnhenn method (*Z. Unters. Nahr.-Genussm.*, 1923, **46**, 154; Abst., ANALYST, 1924, **49**, 105). It is necessary to use pure carbon tetrachloride, to remove the mineral oil after saponification, and to determine the iodine value of the free fatty acids. The method for determining the Burton–Robertshaw index is modified by using 50 ml. of pure carbon tetrachloride, and 4 g. of the sulphated oil, having a Burton–Robertshaw index of about 70 per cent., are taken. After separation the solvent layer is run into a 100-ml. glass-stoppered flask, the separating funnel is washed out, and the contents of the flask are made up to 100 ml. with pure carbon tetrachloride and thoroughly mixed. The solution is dried with anhydrous sodium sulphate and filtered quickly, and the first 25 ml. are rejected. The remainder is collected in a flask, which is stoppered immediately after filtration is complete, and the iodine value is determined on this solution. Eight g. of pure pyridine and 10 g. of conc. sulphuric acid are each mixed separately with 20 ml. of glacial acetic acid, with careful cooling. The solutions are then united and cooled again, 8 g. of bromine (dissolved in 20 ml. of glacial acetic acid) are added, and the whole is made up to a litre with glacial acetic acid. The solution is then about 0·1 N, the stability depending on the purity of the reagents. To standardise it, 20 ml. of 0·1 N arsenious acid solution are run into a flask, acidified with 10 ml. of dilute hydrochloric acid and diluted with 30 ml. of water, after which 5 ml. of chloroform and sufficient aqueous methyl orange solution to give a rose colour are added. The solution is then titrated with the pyridine reagent. The amount of "oily matter" to be used for the determination is found by evaporating an aliquot part of the carbon tetrachloride solution, and a volume that contains 0·1 to 0·2 g. for oils of high iodine value, or 0·6 to 0·8 g. for solid fats, is mixed with 10 ml. of chloroform, and 25 ml. of pyridine reagent are added, with a few drops of glacial acetic acid if the solution is not clear. The reaction is complete in 5 minutes. The stopper is removed, with the usual precautions, 60 ml. of water are added, the flask is shaken, 0·1 *N* arsenious acid solution is run in until the bromine colour is removed, and then, after further shaking, the indicator is added. The contents of the flask are titrated back with the pyridine reagent until the rose colour disappears. The method was applied to sulphated linseed oil, and it was found better to use weighed rather than measured quantities, on account of the high specific gravity. Sulphuric acid could not be substituted for hydrochloric in the determination of the Burton–Robertshaw index. It appears probable that this work may lead to a simplified method of analysing sulphated oils. D. G. H.

Control of the Purity of Tanning Extracts. A. Jamet. (*J. Int. Soc. Leather Trades Chem.*, 1937, **21**, 298–300.)—The following reactions have been investigated:—(i) *Formaldehyde and hydrochloric acid.*—Fifty ml. of a tanning solution of suitable concentration are treated with 5 ml. of pure conc. hydrochloric acid and 10 ml. of 40 per cent. formaldehyde, and the mixture is boiled, under reflux and with a direct flame, for 30 minutes. After thorough cooling, the liquid is filtered. Ten ml. of filtrate are shaken with 1 ml. of 1 per cent. iron alum solution, and then treated, without shaking, with 5 g. of pure crystallised sodium acetate. The precipitate before and after cooling, and the colour of the final liquid, particularly near the sodium acetate crystals, should be observed. The presence together of pyrogallol and catechol tanning agents is indicated by a blue colour.

(ii) *Acetic acid and lead acetate.*—(A)—Five ml. of the tanning solution are mixed with 10 ml. of 10 per cent. acetic acid and 5 ml. of 10 per cent. neutral lead acetate solution. Pyrogallol tannins give a precipitate. (B)—Ten ml. of the filtrate from method (i) are treated with 2 g. of crystallised sodium acetate and 4 ml. of water. When the salt has dissolved, the liquid is mixed with 5 ml. of 10 per cent. neutral lead acetate solution. In methods A and B the bulk of the precipitate, if any, and its colour after shaking and standing, should be observed. The two liquids are then filtered and 10 ml. of each (clear) filtrate are treated with 2 or 3 drops of 10 per cent. iron alum solution. The colours that develop in the upper layer of the liquid after the addition of 1 drop without shaking, and after the second or third drop, both with and without shaking, should be noted. Oak-bark gives no colour, chestnut a light grey, and myrobolans and sumac a violet-blue.

(iii) *Ammonium sulphide.*—(A)—Twenty-five ml. of 2·4 per cent. solution are boiled for 1 or 2 minutes with 2 or 3 drops of conc. sulphuric acid, and the mixture is cooled and treated with 5 g. of crushed ordinary salt, allowed to stand for 10 minutes, with occasional shaking, and filtered. Ten to 15 drops of ammonium sulphide, 15 ml. of water, and 3 ml. of the filtrate are mixed in a test-tube, shaken, and left for 5 minutes. Pyrogallol tannins and mimosa give a precipitate. (B)—Fifteen ml. of 0·4 per cent. tannin solution are treated with 2 ml. of ammonium sulphide and allowed to stand for 15 minutes. The certainty of the results given by this method requires verification. E. M. P.

Molecular Weights of Vegetable Tannins. G. W. Douglas and F. E. Humphreys. (*J. Int. Soc. Leather Trades Chem.*, 1937, **21**, 378–388.)—In order to determine the molecular weight of tannins it is desirable to remove non-tans and salts as far as possible, and to do this an electro-dialysis technique has been evolved by which the smaller particles are eliminated from solutions of vegetable-tanning materials. Solutions of gallotannin, mimosa and quebracho were thus obtained in which 95 per cent., or more, of the soluble matter was tannin. The apparatus consists of ebonite rings supported in such a way that membranes can be placed between them. The ends are closed with ebonite plates and the whole forms a watertight cylinder when clamped together with rubber rings as gaskets, each compartment having a capacity of about 80 ml. Holes are drilled in the bottom and near the top of each of the rings, and each of the end plates is drilled for the insertion of the electrodes. For quantitative work on the residual liquor in the central compartment three chambers are used, with an electrically driven stirrer in the centre one. The solution of tanning material is placed in the centre compartment, which is divided from the other cells by cellophane (0·0008 in. thick, grade 300), and water is placed in the other two cells and renewed from time to time. A potential difference is applied across the two electrodes, and the voltage is altered from time to time, so that the current flowing through the dialyser never exceeds 50 milliamperes. After 7 to 10 days, when no further dialysis appears to be taking place, the residual liquor, which is usually turbid, is examined for soluble substances, tannin, etc., the freezing-point is determined, and the molecular weight is found by the method of Humphreys (*J. Int. Soc. Leather Trade Chem.*, 1934, **18**, 165) from the freezing-point depression. Molecular weights (*a*) before and (*b*) after dialysis were as follows: myrobolans (*a*) 340, (*b*) 1917; mimosa, two samples, (*a*) 603 and 432, (*b*) 1570 and 1704; chestnut (*a*) 462, (*b*) 1545; quebracho (*a*) 1159, (*b*) 2421; quebracho, sulphited, (*a*) 369, (*b*) 763; gambier (*a*) 324, (*b*) 520; gallotannin, two samples, (*a*) 1445 and 1223, (*b*) 3434 and 3084. In order to find the approximate size of the largest particles that would pass through the membranes, solutions of compounds of known molecular weight (sucrose and raffinose) were placed in the centre compartment, and from the results it is concluded that any substance of a molecular weight of 500 or less in the tan liquors investigated would pass through the membranes and be removed. The experiments suggest that most of the vegetable tannins have molecular weights at least as great as 2000, and that the tan liquors examined, with the possible exception of gambier, were mixtures of tannins, containing very large particles having molecular weights exceeding 2000, with considerably smaller ones with molecular weights below about 500. Since the molecular weights found are greater than would be expected from propounded formulae, it is suggested that the actual tannin molecules are built up of a number of simpler compounds. D. G. H.

Anti-oxidant Properties of the Tocopherols. H. S. Olcott and O. H. Emerson. (*J. Amer. Chem. Soc.*, 1937, **59**, 1008–1009.)—In order to ascertain the relationship between the inhibitols (*J. Biol. Chem.*, 1936, **113**, **319**) and tocopherols the three tocopherols and their allophanates were assayed for anti-oxidant activity by the oxygen-absorption method (*Ind. Eng. Chem.*, 1935, 27, 724). Like the concentrates from wheat germ and cotton-seed oil (ANALYST, 1937, 62, 50) the tocopherols were found effective anti-oxidants in lard and in oleo oil, but they had no activity in esters prepared from hydrogenated cotton-seed oil. The inhibitols obtained from lettuce and tomatoes (ANALYST, 1935, 60, 111) in the methanol fraction, after distribution between petroleum spirit and 92 per cent. methanol, are, presumably, not tocopherols. The α-, β- and γ-tocopherols were found to be increasingly effective as anti-oxidants in the order α, β, γ, but as vitamin *E* β is less effective than α or γ, and this lack of correlation between anti-oxidant and vitamin properties may explain the previously observed lack of direct relationship in the concentrates. Simple esters of the tocopherols are effective as the vitamin, but ineffective as anti-oxidants. The tocopherol allophanates were still more effective anti-oxidants, and this somewhat unexpected fact suggests that the activity of the allophanates runs parallel with that of the parent compounds. Since all the anti-oxidants of known structure are phenolic in nature, the tocopherols may belong to the same class. Their absorption spectra resemble that of hydroquinone; they have, however, only feeble acidic properties or none. D. G. H.

Inorganic

Application of Formaldehyde in Volumetric Analysis. D. Tschawdarov. (*Z. anal. Chem.*, 1937, **109**, 396–402.)—The stability of oxymethanesulphonic acid can be utilised in oxidimetric determinations in which sulphurous acid or a sulphite has been used as a reducing agent. The author has applied the principle to the volumetric determination of iron by means of permanganate or dichromate after reduction of the ferric chloride with alkali sulphite or bisulphite and treatment of the reduced solution with formaldehyde. W. R. S.

2, 4-Dihydroxyacetophenone as a Qualitative Reagent for Ferric Iron. S. R. Cooper. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 334–335.)—The reagent is prepared and purified according to the method of Necki and Sieber (*J. prakt. Chem.*, [N.S.], 1880, **23**, 147). Three parts by weight of anhydrous zinc chloride are dissolved in 3 parts by weight of glacial acetic acid, and to the solution 2 parts by weight of resorcinol are added. The mixture is heated to b.p. (145°–150° C.) on a sand-bath, the source of heat being then removed and the reaction left to complete itself. The crystalline compound separates on diluting the mixture; and the crystals are washed with cold dilute hydrochloric acid, and further purified by several treatments with dilute hydrochloric acid and animal charcoal, boiling, filtering, cooling and crystallising. The m.p. of the white needles is 142° C., and an alcoholic solution is made for use by dissolving 10 g. in 100 ml. of 95 per cent. ethyl alcohol. One ml. of the iron solution to be tested is placed on a colourless watch-glass, 2 drops of reagent are added, and the colour is compared with that of 1 ml. of the solution and 2 drops of alcohol. The limit of sensitivity was 0·002 mg. of iron in 1 ml. of solution, or 2 parts of iron in 1,000,000 parts of solution; at that dilution the red tint is faint, whereas 0·0022 mg. gives a very slight, and 0·0033 mg. a light red colour. Mercurous, mercuric, aluminium and manganese salts give a precipitate with the reagent, and copper, cobalt, nickel and chromium salts interfere with the reaction, owing to their colour. However, iron can still be detected in a solution containing 300 times as much copper, 1800 times as much cobalt, 400 times as much nickel, 25,000 times as much manganese, 30,500 times as much mercurous mercury, 11,440 times as much mercuric mercury, 32,500 times as much aluminium and 225 times as much chromium. In solutions of ordinary analytical strength (10 mg. of metal ion per ml.) ferric iron can be detected in the original solution, since aluminium, mercurous, mercuric and manganese salts do not precipitate before the red colour has appeared. The acidity of the solution may be approximately 0·06 *N* in hydrochloric and nitric acids, and 0·03 *N* in sulphuric acid, without affecting the sensitiveness of the test, but, if strongly acid, the solution should be neutralised to the point of incipient precipitation with ammonium hydroxide. Oxalates, tartrates, and citrates interfere with the reaction and phosphates must not be present, but sugar and glycerol have no effect. D. G. H.

Separation of Gold from Tellurium. J. Seath and F. E. Beamish. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 373–374.)—Hydroquinone, which acts as a precipitant of gold (*cf.* ANALYST, 1937, 494), was found to effect its quantitative separation from tellurium. Selenium is co-precipitated to a certain extent, though the small amount occluded in the gold is volatilised on ignition. For the separation of gold from tellurium, the chloride solution is adjusted to 1·2 *N* acidity, brought to incipient boiling, and gradually precipitated with a slight excess of 0·5 per cent. hydroquinone solution. Boiling is continued for some minutes until the gold has coagulated. The precipitate is collected in a porous porcelain crucible, washed with water, ignited, and weighed. The filtrate is adjusted to 4 *N* acidity with hydrochloric acid and precipitated by the customary procedure with sulphur dioxide and hydrazine hydrochloride. The precipitate is washed with water until free from chloride, and dried at 105° C. for 45 minutes in an atmosphere of carbon dioxide. By adopting this mode of treating the tellurium precipitate and omitting the washing with alcohol prior to drying, the authors avoid the positive error commonly involved in tellurium determinations. W. R. S.

Quantitative Determination of Aluminium by Precipitation with Urea. H. H. Willard and N. K. Tang. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 357–363.)—Alumina is quantitatively precipitated from a sulphate solution approximately neutralised with ammonia, and treated with 4 g. of urea and 20 g. of ammonium chloride, by 2 hours' boiling after the liquid has become opalescent. After settling, the precipitate is collected, and the washed beaker is rinsed with a little hydrochloric acid, the small quantity of adhering alumina being recovered by precipitation with ammonia and added to the bulk of the precipitate. This is washed with 1 per cent. ammonium chloride solution containing a slight excess of ammonia (methyl-red indicator). The precipitate is ignited to constant weight in a platinum crucible at 1200° C., which removes the sulphur trioxide retained by the precipitate. Aluminium can be separated from bivalent metals by single or double precipitation with urea from succinate solution. The hot chloride solution is nearly neutralised with ammonia, treated with succinic acid (5 g.), ammonium chloride (10 g.), and urea (4 g.), diluted to 500 ml. (for 0·2 g. of alumina), and gently boiled for 2 hours after it has become turbid. The basic succinate precipitate is collected and washed as described above, but the small precipitate obtained after cleaning the beaker with acid is collected separately. The precipitate is dissolved, if required, in hot dilute hydrochloric acid, and the precipitation is repeated. The separation from calcium, barium, magnesium, manganese, and cadmium was complete in one precipitation. The separation from nickel, cobalt, and zinc by double precipitation is very satisfactory, and more effective than double precipitation with ammonia. Cupric salt should be reduced to the cuprous state by boiling with hydroxylamine hydrochloride or ammonium bisulphite prior to the precipitation of the aluminium. Iron also may be separated from aluminium by the above procedure (double treatment) after reduction to ferrous salt by boiling with phenylhydrazine (2 ml.). W. R. S.

Volumetric Determination of Aluminium in Magnesium Alloys. A. E. Martin. (*J. Soc. Chem. Ind.*, 1937, **59**, 179T–180T.)—The following methods depend on the titration of the solution of the aluminium salt with standard alkali. *Electrometric titration.*—A 0·24-g. sample of the alloy is dissolved, by heating, in 25 ml. of *N* sulphuric acid; 4·5 ml. of *N* sodium hydroxide solution are added to neutralise most of the excess of acid, and the solution is diluted to 200 ml. Equal volumes of this solution are placed in two beakers, and a slight excess of quinhydrone is added to each. The solutions are connected electrically by a potassium chloride-agar bridge, and platinum foil electrodes are immersed in each solution and connected with a galvanometer (preferably 700 ohm, 1600 mm. per microamp.) through a 1 megohm resistance, this series resistance being altered, if necessary, so that a suitable deflection is obtained during the course of the titration. One solution is the reference solution. The other solution is stirred mechanically and titrated with 0·05 *N* sodium hydroxide solution. As the titration proceeds the galvanometer deflection changes at first rapidly, then slowly, and finally rapidly again, as can be shown by plotting a titration curve. The volume of alkali used during the period of relatively slow change of deflection is that taken in the titration of the aluminium. Solutions containing known amounts of aluminium are titrated for the purpose of standardisation, and a titration must also be carried out with a magnesium solution containing no aluminium to allow for a small "blank," which must be deducted from the titration result with the sample. The applicability of the method to an alloy containing 5 per cent. of aluminium is mentioned, but no indication is given of the order of accuracy or of the effect of other alloying elements.

Titration with indicators.—Use is made of two indicators which change colour close to *p*H 3·7 and *p*H 6. A 1-g. sample is dissolved in 9 ml. of conc. hydrochloric acid. The solution is diluted to about 200 ml., two drops of bromophenol blue are added, and the excess of acid is neutralised with *N* sodium hydroxide solution until the indicator becomes colourless; 10 drops of *N* hydrochloric acid are then added immediately, and the solution is diluted to 250 ml. To a 25-ml. portion of the solution contained in a Nessler glass are added 2 drops of bromophenol blue indicator, and the liquid is titrated with 0·1 *N* sodium hydroxide solution, drop by drop, until the indicator becomes colourless (on the verge between a faint yellow and a faint blue). One drop of methyl-red indicator is added, and the titration is continued until a sharp colour change from red to a "neutral" tint occurs.

Standardisation against solutions containing known amounts of aluminium is required, and a "blank" on an aluminium-free magnesium solution must be deducted. It is stated that the colour changes of the indicators need to be followed in daylight; also that to obtain reliable results the correct amount of each indicator must be used. (The strengths of indicator solutions are not given.)

S. G. C.

Determination of Zirconium by Precipitation as Arsenate. W. C. Schumb and E. J. Nolan. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 371–373.)—Ammonium arsenate was found to be a satisfactory reagent for the quantitative precipitation of zirconium, being more accessible than organic arsenic derivatives (*e.g.* ANALYST, 1937, 495) and preferable to sodium arsenate (*id.*, 1928, **53**, 458) on account of the ready elimination of combined and adsorbed reagent from the precipitate, brought about by reduction with carbon during ignition with the filter-paper. Quantitative precipitation of zirconium arsenate takes place in acid (2·5 *N* hydrochloric or 3·75 *N* nitric) solution. The interfering elements are thorium, titanium, cerium, tungsten, tantalum, and niobium, it being understood that hafnium is precipitated and weighed with the zirconia. Tungsten, tantalum, and niobium are removed by a preliminary (single or double) fusion with potassium carbonate; the interference of thorium, titanium and cerium is overcome by double precipitation and a colorimetric determination of titania in the weighed zirconia.

For the determination of zirconium in minerals the fine powder (equivalent to not more than 0·1 g. of ZrO_2) is fused with sodium (potassium) carbonate; extraction with water removes phosphorus and tungsten (earth acids). The residue from the previous fusion is fused with bisulphate. The filtered solution of the melt is precipitated with ammonia; the precipitate is collected, washed and dissolved in 82 ml. of strong hydrochloric acid and 100 ml. of water. The cold solution is diluted to 360 ml., stirred, and treated with 50 ml. of 1 per cent. ammonium arsenate, added drop by drop. The liquid is heated and kept boiling for 20 minutes, and 15 ml. of 10 per cent. ammonium arsenate solution are added from a burette. The hot solution may be filtered at once, the beaker being cleaned with *N* hydrochloric acid. The precipitate is washed and returned to the beaker with hot water. The suspension is evaporated on the water-bath until pasty and treated with 82 ml. of strong hydrochloric acid, which is poured over the filter last used; the paper is then rinsed with 100 ml. of water, which is reserved. The precipitate is dissolved by exactly 5 minutes' boiling with the acid, after which the reserved wash-water is added. The liquid is diluted to 360 ml., left to cool, and again precipitated with dilute arsenate solution as described above; it is boiled and treated with 10 (not 15) ml. of strong arsenate solution. The precipitate is collected on a double filter and washed with *N* hydrochloric acid followed by hot water, transferred to a tared porcelain crucible, and dried in an oven. The paper is ashed with the full flame of a Bunsen burner while the crucible is in an upright position. The crucible is then tilted and the last of the carbon burned away. It is then covered with a porcelain lid, except for a small open slit, and heated in an upright position with the full flame of a Méker burner for an hour. After cooling, the ignited precipitate is weighed as ZrO_2, which is tested colorimetrically for titania.

W. R. S.

Volumetric Determination of Hydrogen Peroxide by Means of Potassium Bromate. L. Szebellédy and W. Madis. (*Z. anal. Chem.*, 1937, **109**, 391–396.)—In the presence of manganous salt as a catalyser, hydrogen peroxide reacts with bromate according to the equation $3H_2O_2 + HBrO_3 \rightarrow 3H_2O + HBr + 3O_2$. If no catalyser is added, the interfering reaction $5HBr + HBrO_3 \rightarrow 3Br_2 + 3H_2O$ sets in when sufficient hydrobromic acid has been formed. The neutral solution of hydrogen peroxide is made up to 25 ml., and treated with 1 g. of crystallised manganous chloride followed by 25 ml. of *N* hydrochloric acid. The liquid is then titrated with 0·1 *N* potassium bromate solution until it turns pale yellow (within 0·5 to 1 ml. of the end-point) and warmed to 40° C. When effervescence has ceased, the bromate solution is added, drop by drop, at intervals of 15 to 20 seconds until a single drop imparts a stable yellow colour to the solution.

W. R. S.

Volumetric Determination of Small Amounts of Selenium by Oxidation in Colloidal Solution. W. C. Coleman and C. R. McCrosky. (*J. Amer. Chem. Soc.*, 1937, **59**, 1458–1460.)—Selenium in colloidal solution can be oxidised rapidly and quantitatively with volumetric oxidants. It can be titrated with potassium bromate in the presence of a strong acid (*cf.* Szebellédy and Schick, *Z. anal. Chem.*, 1934, **97**, 186–191; Abst., ANALYST, 1934, **49**, 571). Test analyses of standard sodium selenocyanate solution containing excess of sodium cyanide were made. After the addition of a 1 per cent. solution of gum arabic (1 ml. per 10 mg. of selenium), the solution was acidified with hydrochloric acid until of *N* strength, hydrogen cyanide was removed by aspirating air rapidly through the liquid for 15 minutes, and the selenium was titrated with potassium bromate to a colourless end-point. The average error in twenty determinations was less than 0·2 per cent. Colloidal selenium is oxidised by iodine monochloride according to the equation

$$Se + 4ICl + 3H_2O \rightarrow H_2SeO_3 + 2I_2 + 4HCl.$$

This reaction has been used to obtain a sharper end-point in the above determination, by the addition of 4 ml. of carbon tetrachloride and sufficient iodine monochloride to oxidise the remaining selenium just before the end of the titration. Flasks with ground-glass stoppers are best for the completion of the reaction (*cf.* Swift and Gregory, *J. Amer. Chem. Soc.*, 1930, **52**, 804). If less than 10 mg. of selenium are being determined, gum arabic can be omitted and a sharper end-point obtained. Air is aspirated through the solution for not longer than 10 minutes and a solution of acidity from 4 *N* to 6 *N* is used for the titration. After oxidation of colloidal selenium with iodine monochloride the liberated iodine can be titrated with *N*/10 potassium bromate solution; 4 ml. of carbon tetrachloride are added before the complete oxidation of the iodine. The average error for six determinations on solutions containing from 0·01077 to 0·02194 g. of selenium was less than 0·3 per cent.

With acid solutions of potassium iodate, the following reactions occur:

$$5Se + 4IO_3' + 3H_2O + 4H^{\cdot} \rightarrow 5H_2SeO_3 + 2I_2$$
$$2I_2 + IO_3' + 6H^{\cdot} + 5Cl' \rightarrow 5ICl + 3H_2O$$

The selenium is oxidised by four-fifths of the iodate solution required for complete titration. The remaining iodate discharges the colour of the iodine that was liberated. Thus potassium iodate may be substituted for bromate in the iodine monochloride titration. Other oxidising agents were not satisfactory. It is suggested that this method may be adapted to the determination of selenium in glass, rubber, or any material from which it can be precipitated as free selenium.

E. B. D.

Microchemical

Quantitative Drop Analysis. VII. Further Investigations on the Determination of Calcium. R. Lindner and P. L. Kirk. (*Mikrochem.*, 1937, **22**, 291–300.)—Further investigation of the method for the determination of calcium previously described (*Mikrochem.*, 1933, **14**, 15; Abst., ANALYST, 1934, **59**, 64) shows that a balance of errors existed, and that whilst the sample of diphenylamine used gave excellent end-points, other samples were not dependable. An improved procedure is given, suitable for the determination of 0·5 to 12γ of calcium, in sample solutions and in blood, with a relative error of less than ± 0·5 per cent. on all but the lowest amounts. The ceric sulphate method is used with back-titration with standard ferrous ammonium sulphate, phenanthroline ferrous sulphate being used as indicator. The general technique and apparatus are those previously described (*loc. cit.*). *Reagents.*—All water is re-distilled in glass; sulphuric acid is also re-distilled in glass. (1) Ammonium oxalate (4 per cent. solution) filtered through a layer of fine asbestos on a sintered glass filter. (2) Saturated sodium acetate solution, filtered through a sintered glass filter. (3) Asbestos: Italian, medium fibre, washed, ignited, ground moderately fine in a mortar; this is boiled with acid ceric sulphate solution and washed with re-distilled water on a sintered glass filter; a suspension is prepared. (4) Wash solution, prepared by saturating a 1 : 10 solution of ammonia with freshly precipitated and washed calcium oxalate, and filtering this solution, before use, through a sintered glass filter with asbestos mat. (5) 0·01 *N* Ceric sulphate solution; this must be made from ceric sulphate free from organic contamination. (6) 0·01 *N* Ferrous ammonium sulphate, in 0·1 *N* sulphuric acid. (7) Indicator solution: a 0·025 *M* solution of phenanthroline ferrous sulphate, prepared according to the method of Walden, Hammett and Chapman (*J. Amer. Chem. Soc.*, 1931, **53**, 3908) and diluted 1 to 10 to give a concentration of 0·0025 *M* per litre. *Detail.*—Biological material must first be ashed, and the ash dissolved in 1 drop of 0·1 *N* hydrochloric acid, and transferred with a capillary pipette to a small porcelain dish; while an inorganic solution may be measured at once into the dish, a small amount of hydrochloric acid then added, and the thread stirrer inserted. A volume of the ammonium sulphate solution equal to that of the sample is added, with stirring, the basin being kept on a small hot-plate. About 0·1 ml. of the sodium acetate solution is added, and digestion is continued for about 5 minutes, water being added, if necessary, to maintain the volume. After standing overnight the calcium oxalate is filtered into a filter-stick of 1·5-mm. external diameter, covered with a thin layer of asbestos. The dish and precipitate are washed with 30 drops of wash-liquid, and the pad is washed back into the dish with 6 *N* sulphuric acid. After the liquid has been heated for 2 minutes and cooled for 5 minutes, a measured amount of ceric sulphate (5) in excess of the oxalate is added, and the solution is stirred for 3 minutes. A drop of the indicator solution is added, and the ceric sulphate is back-titrated with the ferrous ammonium sulphate (6). The result is subtracted from that obtained in a control test with the reagents. J. W. M.

Determination of Uranous and Uranic Oxides in Different Layers of a Uraninite Crystal. E. Gleditsch and R. Bakken. (*Mikrochem. Acta*, **1937**, **1**, 83–86.)—Layers of a single crystal of uraninite (a clevite from Norway) are separated mechanically by means of fine steel forceps and by chipping off tiny pieces along the crystalline faces. The proportion of uranous and uranic oxides was determined in three layers of one crystal by the following method:—About 0·5 g. of mineral is dissolved by heating it with sulphuric acid and adding water until the solution contains 10 per cent. of sulphuric acid. The uranous oxide present is determined by titration with 0·01 *N* permanganate solution. The liquid is reduced in a Jones reductor and the uranium is then oxidised to the quadrivalent state by blowing clean air through the solution for five minutes. A new titration with permanganate gives the total uranium, and from this the uranic oxide is deduced. The highest UO_2/UO_3 value is in the core, and it diminishes towards the outside; the same thing applies to uranous oxide content, whilst the percentage of uranic oxide is highest outside and lowest in the core.

J. W. M.

Microchemical References. (Supplement to *Mikrochem.*, **1937**, **22**, pp. 109.) —References to recent literature (1936 and 1937) are arranged in the alphabetical order of the subjects referred to, instead of, as in previous issues, in alphabetical order of the authors under very wide subject headings. J. W. M.

Physical Methods, Apparatus, etc.

Nephelometric End-point in Atomic Weight Titrations. A. F. Scott and F. H. Hurley. (*J. Amer. Chem. Soc.*, **1937**, **59**, 1297–1302.)—The well-known Harvard method for determining atomic weights by the analysis of pure halogen compounds is essentially a titration process in which the halide ion in the analytical sample is precipitated by silver ion, the end-point being found by nephelometric tests. In making these tests of the relative amounts of silver and halide ions left in the solution after the precipitation of the bulk of the silver halide, two small equal samples of the solution are withdrawn; the halide in one is precipitated as silver halide by addition of silver ion, and the silver-content of the other is determined, also as silver halide, by precipitation with halide ion. The precipitates form because of the common-ion effect and, being small in amount, remain in suspension for some time. The turbidity or opalescence so produced has been assumed to be proportional to the concentrations of halide and silver ion, respectively, in the sample solutions. In accordance with this assumption, the equivalence of silver and halide in the titration process is assumed to have been attained when the corresponding opalescences of "excess silver" and "excess halide" of the test samples are equal. The validity of the end-point thus found with solutions which have come to equilibrium at room temperature appears to be fully substantiated. Some doubt exists as to whether this is also true for silver chloride titration-solutions which have been cooled on ice to reduce the solubility of the silver chloride. It has been found, for example, that water acidified with nitric acid and saturated with silver chloride at 0° C. does not give the same opalescence on treatment with silver ion and chloride ion respectively. The reason adduced by the authors is that silver chloride is slightly more soluble in solutions containing excess of chloride than in those containing a similar excess of silver. Thus less material would be precipitated in presence of excess of chloride than in presence of excess of silver. At relatively high concentrations of silver chloride, such as are present in solutions at room temperature, the amount of silver chloride left in solution after addition of either ion would be small in relation to the amount of silver chloride precipitated; hence the opalescence would be similar in each instance. On the other hand, with smaller concentrations of silver chloride, as in the cold solution, the difference would become significant, and the "excess chloride" suspension, having less material in suspension, would show less opalescence than the corresponding "excess silver" suspension. Colloidal silver chloride, which is frequently present in the original titration liquid, is considered to reduce the error due to the above-mentioned cause. S. G. C.

Fluorescence Test for Molybdenum. L. Szebellédy and J. Jónás. (*Mikrochem. Acta.*, 1937, 1, 46–50.)—Cochineal tincture may be used for the detection of molybdenum. The test is made at *p*H 5·7 to 6·2, at which reaction molybdenum gives a fiery-red fluorescence. The test is very sensitive, but is only applicable to a limited extent, owing to the fact that the following cations interfere: lead, mercury, copper, bismuth, cobalt, nickel, iron, manganese, chromium, aluminium and magnesium. The following do not interfere: silver, cadmium, arsenic, antimony, tin, zinc, calcium, strontium, barium, potassium, sodium and ammonium. Vanadates interfere, but tungstates do not. J. W. M.

Thermal Analysis of Rare-Earth Nitrate Mixtures. L. L. Quill, R. F. Robey and S. Seifter. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 389–392.)—It is suggested that thermal analysis may be used for the quantitative analysis of mixtures of the rare earths. The authors determined the rate of cooling of fused binary mixtures of samarium magnesium nitrate and bismuth magnesium nitrate, of the double magnesium nitrates of two members of the cerium group, and of the simple nitrates of two such members. The mixtures were found to form a continuous series of solid solutions. As the authors remark, it is obviously necessary to investigate ternary and quaternary systems before the method can find practical application. W. R. S.

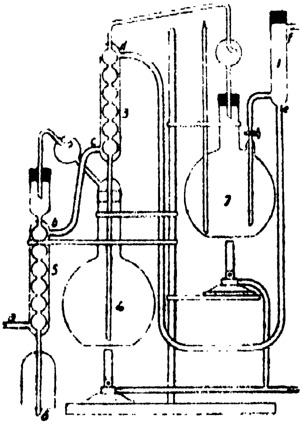
Examination of Precious Stones. J. Bolman. (*Chem. Weekblad*, 1937, 34, 496–501.)—Goniometric measurements and determinations of sp.gr. or of refractive index usually serve to distinguish genuine stones from glass imitations, but are inadequate when the specimen is a "synthetic" stone, or when two genuine stones from different localities are in question. In such event the polarising microscope may provide useful information, particularly if inclusions (either solid, liquid or gaseous) are present, as these are frequently very characteristic;

a magnification of × 165 is convenient. Thus, Burma rubies contain needle-shaped crystals of rutile, single or in bundles, whilst "canals" due to liquid inclusions are characteristic of Ceylon rubies, and synthetic rubies contain only very small air bubbles. Columbia (Muso) emeralds contain rhombohedral-shaped calcite crystals, air bubbles, and large liquid canals, whilst in emeralds from the Ural districts the liquid inclusions are smaller and shining blade-shaped crystalline inclusions are visible. The zone-structure which may be seen on the facets of certain crystals also serves to distinguish certain genuine and synthetic stones; thus, it is more marked on synthetic sapphires than on the natural stones. The colour of the stone is also occasionally a useful guide, and an apparatus (the "Detectoscope") for evaluating it is described. The stone is placed over an aperture in a box in which is a weak source of light and five colour-filters of different wave-length, each of which may be brought between the source and the stone at will. Provision is made for viewing the stone from above through a lens or polarising microscope, and suitably-shaped diaphragms serve to exclude extraneous light. Other optical methods are fluorescence analysis in ultra-violet light (*cf.* Grant, ANALYST, 1937, 731); the use of the refractive index to ascertain whether diamonds have been ground or cut; and the use of photographs of reflection-and refraction-effects to identify a particular precious stone in terms of the way in which it is cut. The last method is intended to provide a means of safeguarding the owner of a stone against substitution, *e.g.* by a jeweller commissioned to set it. The original paper is fully illustrated. J. G.

Risks of Fire or Explosion in Operating Theatres. J. H. Coste and C. A. Chaplin. (*Brit. J. Anaesthesia*, 1937, **14**, 115–129.)—The limits of explosion of mixtures of (*a*) ethyl chloride vapour and air, and of ether vapour with (*b*) air, (*c*) oxygen and (*d*) nitrous oxide, were found to be between: (*a*) 5 to a little over 15 per cent. by volume of ethyl chloride, (*b*) 2 to 8 per cent. of ether vapour, (*c*) 2 per cent. (the lower limit only was investigated, and the value given confirms that found by other workers), and (*d*) 1·5 to 16 per cent. of ether vapour. The procedure was to pass a spark between two brass wire electrodes in the centre of a cylindrical tinned-iron canister (capacity 7 litres) in which the mixture was made. The hydrochloric acid produced by the combustion of ethyl chloride was found to be extremely irritant. Gas mixtures from two forms of Boyle's apparatus (one the bubbling type, and the other of the design in which the gas impinges on a saturated wick in a vessel of ether) and consisting of ether, nitrous oxide and oxygen, ether and oxygen, or ether, chloroform and oxygen, were shown to be either explosive or combustible; exceptions were mixtures of nitrous oxide and oxygen. Even after prolonged use of ether for open-mask anaesthesia the concentration of ether in a normal operating theatre was found to be very small; the air at 2 inches from the patient's mouth was non-explosive, and the proportion of ether fell off very rapidly as the distance from the patient increased. These results are attributed to the rapid descent of ether vapour through the air. If ether is spilt on the floor (*e.g.* by the breakage of a bottle) and the vapour cannot spread laterally, the concentration of ether in the air varies regularly from saturation (*i.e.* 40 per cent., a combustible but non-explosive mixture) at 1 inch above the surface, to 3.35 per cent.

(an explosive mixture) 11 inches higher. These conditions might be expected when the volume spilt is sufficient to saturate the air of the room, and uniform and restricted ventilation is provided all round the walls at a height of 1 foot. The low ether-content of air in a small room in which ether is spilt is very low, because of the lateral spread and density of the vapour, and because the formation of the vapour cools the liquid; at 1 inch above the pool the air is explosive, but the concentration is very small 7 inches higher up. The Pregl micro-method of combustion was used to determine the amount of ether present in air, modifications being adopted which served to introduce the sample at a suitable speed into the main oxygen-stream without contact with lubricant which might absorb ether. A technique has also been evolved for the collection and storage, without alteration, of samples of mixtures of air and ether or other vapours; mercury cups with gas tubes, also containing mercury, were suspended at intervals in a cylinder, 15 inches high, which was placed over the surface of evaporation, and sampling was effected by lifting the appropriate tube. J. G.

Apparatus for the Preparation of Doubly-Distilled Water. E. C. H. J. Noyons. (*Chem. Weekblad,* 1937, 34, 434.)—Tap water supplied to the flask 2 is boiled, the steam being conducted through a splash-head to a condenser 3, where it is condensed and falls into the flask 4. Here it is again boiled and is re-condensed in 5 and collected in the receiver 6. Each flask should contain a device to stop bumping. The cooling-water enters the condenser 5 at *a* and leaves it at *b*, and then serves the condenser 3 via the inlet *c* and the outlet *d*. It is then conducted to the regulator 1, and feeds the flask 2 at such a rate as to keep the level constant without preventing the contents from boiling; this is achieved by adjustment of the tap shown, *f* being an overflow. Back-pressure effects are eliminated by means of a vertical tube drawn out to a jet at one end, the other being inserted in the flask 2 as shown. J. G.



Reviews

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Vol. XVI; Editor: J. R. JOHNSON; pp. v + 104. Vol. XVII; Editor: L. F. FIESER; pp. v + 112. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 8s. 6d. net each volume.

The books in this series need no introduction to those actively engaged in the pursuit of organic chemistry. For others, it may be well to reiterate that the characteristic feature of these publications is that the details of the preparations set out have been tested by workers independent of the originators, and that all are thus, so to speak, guaranteed "to work."

The sixteenth volume includes twenty-eight, and the seventeenth volume thirty preparations, each of which is arranged in the usual way.

The compounds dealt with are, from several points of view, a very interesting group, some being the starting materials for the preparation of important substances and others forming a series which would be useful to teachers of advanced organic chemistry. Incidentally, a study of the methods employed would form a useful addition to the education of those wishing to take up organic research.

Among the more interesting compounds in Vol. XVI may be mentioned the hydrochlorides of both symmetrical and unsymmetrical dimethyl hydrazines, phthalide, tetrahydrofuran and symmetrical trithiane. The compounds in Vol. XVII are equally varied in type, as may be judged from the following random selection:—Amino-butyric and -caproic acids, butadiene, cellobiose, dihydrochollesterol, β-naphthoic acid, β-naphthoquinone, pentaerythrityl bromide and *d*- and *l*-α-phenylethylamine.

Owing to the wide range of compounds listed the teacher of advanced organic chemistry will find usable examples of many general reactions; thus dehydration is represented by the preparation of aconitic acid from citric acid, Gabriel's phthalimide reaction by the preparation of γ-amino-butyric acid, diazotisation and reduction by the preparation of 1 : 2-amino-naphthol, the cracking of hydrocarbons by the preparation of 1 : 3-butadiene. Other equally interesting examples are also plentiful in the text.

Each volume ends with a list of later references to preparations in preceding volumes, with additions and corrections, and a general subject index to the volumes from X to XVI or XVII, respectively.

Both volumes maintain the high standard of their predecessors, and are well worth the attention of all connected with the production of organic chemicals.

HAROLD TOMS

FIELD TESTS FOR MINERALS. By E. H. DAVISON, B.Sc., Head of The Department of Geology and Mineralogy, School of Mines, Camborne. Pp. viii + 60, with 12 plates. London: Chapman & Hall, Ltd. 1937. Price 7s. 6d. net.

In writing this book, the author, a geologist and mineralogist of long experience, has had in mind the prospector and field geologist rather than the chemist.

The book opens with a section on blowpipe analysis, including closed and open tube tests, tests on charcoal and on plaster tablets, bead tests, flame tests, and other tests sufficiently simple to be carried out under field conditions. Tests for some of the rarer elements, such as vanadium, niobium, selenium, thallium, tellurium, thorium, and cerium, are included.

Subsequent sections deal with the recently developed "spot" tests, using organic reagents, and with microchemical tests depending on the formation of characteristic crystalline compounds.

Next follows a section dealing with the physical properties exhibited by hand specimens of minerals, including specific gravity, hardness, and so on, but not including a detailed treatment of crystallography. This section has twelve plates illustrating mineral structures, and is followed by tables showing the characteristic properties of minerals, arranged according to lustre and in order of hardness.

Many of the organic "spot" tests are very sensitive, and their use in a routine manner, by workers who may have little chemical experience, should be accompanied by a due amount of caution. One feels that perhaps too little stress has been laid on the fact that some of the tests described are influenced by the presence of elements other than the one sought. However, a more intimate understanding of these tests may be acquired by reference to The British Drug Houses' book on "Spot" Tests, mentioned by the author on page 20. Furthermore, by insisting that final conclusions shall not be drawn until all the tests have been employed, the author discourages any tendency to base final conclusions upon the results of isolated tests.

Geologists, and others interested in minerals, will find this book to be of great practical value. The chemist concerned with mineral analysis will also find the book useful, though he may hesitate to base a report on these tests, without confirmation by chemical analysis. C. O. HARVEY

ABSORPTIONS-SPEKTROSCOPIE IM ULTRAVIOLETT. I. ABSORPTIONS-SPEKTRA DER EIWEISS-KÖRPER, KOHLENHYDRATE UND FETTE EINSCHLIESSLICH IHRER AUFBAU- UND ABBAU-SUBSTANZEN. By DR. FRIEDRICH ELLINGER. Pp. 291–343. The Hague: Verlag Dr. W. Junk. 1937. Price 5 (Dutch) florins.

This small volume is actually a reprint from Vol. XII of *Tabulae Biologicae*, and consists principally of 188 ultra-violet absorption-curves based on data obtained from the literature of the subject and showing the relationship between the logarithms of the absorption coefficients and the wave-lengths of the radiations used. The first one-and-a-half pages, however, are devoted to a brief general description of the meaning of the curves and the method of interpreting them, but, apart from this, there is no explanatory matter. The book is therefore essentially a work of reference, and as such will undoubtedly prove of considerable value to workers in this branch of the subject, especially as full and numerous references are given to the sources of information.

As the title indicates, the present volume is the first of a series. It is divided into three main sections dealing with the proteins, carbohydrates and fats, and their related compounds. These sections are further subdivided; thus under the proteins are to be found the unit molecules of the protein structure (aliphatic and cyclic amino acids), the true proteins (*e.g.* albumin, globulin, etc.), gelatin, nucleoproteins, chromoproteins and the substances produced by denaturing proteins, *e.g.* with acids, bases, alcohol or α-particles. The decomposition products of the proteins dealt with include the albumoses and peptones, and substances having the characteristics of amines (*e.g.* the alkylamines, diamines, neurines and guanidines). In a few instances the influence on the curves of the solvent or of the *p*H value of the medium is demonstrated.

The carbohydrates are classified into monosaccharides, disaccharides, products resulting from hydrolysis (*e.g.* invert sugar), osazones, glucosazones and degradation products, such as alcohols, acids and aldehydes; a few miscellaneous substances related to the sugars (*e.g.* cellobiose and lignin) are also included.

The fats comprise neutral animal and vegetable fats and fatty acids, and acrolein and vaseline are included in this section. Cephalin represents the phosphatids, and the common sterols and the products produced from them by irradiation (including lumisterol and vitamin-D_2) are also dealt with.

Since the book is a reprint, there are no indexes, but reference to any particular compound is facilitated by the method of classification adopted, while the references are arranged in the alphabetical order of the authors' names at the conclusion of each of the three sections.

JULIUS GRANT

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms on Wednesday, October 6th, 1937, the President, Dr. G. Roche Lynch, in the chair.

Miss M. B. Elliott, M.B.E., was nominated as an honorary member of the Society.

Certificates were read in favour of Donald Colin Malcolm Adamson, A.I.C., B. Boas, B.Sc., Ernest Oddy, Gerard Lionel Ransome, B.Sc., A.I.C., and Reginald Frank Wright, B.Sc., A.R.C.S., F.I.C.

The following were elected members of the Society:—John Short Dunn, B.Sc., A.I.C., and Ernest Turner, B.Sc., F.I.C.

The following papers were read and discussed:—"Fluorine in Food Products," by H. C. Lockwood, B.Sc., F.I.C.; "Analysis of Coffee Infusions," by F. W. Edwards, F.I.C., and H. R. Nanji, Ph.D., D.I.C., F.I.C.; "The Determination of Tannins in Cacao Kernel," by D. W. Duthie, M.A., Ph.D., A.I.C.

Death

With deep regret we record the death on November 6th of Dr. J. Augustus Voelcker, C.I.E. An obituary notice will be published later.

Obituary

JOSEPH HAROLD TOTTON

By the unexpected death of Joseph Harold Totton on September 7th, at the comparatively early age of fifty-seven, the Society loses one of its most distinguished members in Northern Ireland.

Totton received his early chemical training at Queen's College, Belfast, and took the degrees of B.A. and B.Sc. at the old Royal University of Ireland. Having decided to specialise in analytical chemistry he went to England and became an assistant to the late Colonel C. E. Cassall, Public Analyst for Kensington. In 1907 he passed the examination for the Associateship of the Institute of Chemistry, and later became a Fellow.

On his return to Ireland in 1907 Totton was appointed Public Analyst and Official Agricultural Analyst for County Armagh; later he was elected to the corresponding posts for the City of Belfast, for County Derry (1910) and for County Antrim (1923). As these were all part-time appointments, he was also able to engage in consulting work, and for many years, until his death, was senior partner in the firm of Totton and Hawthorne.

Notwithstanding the claims of his official work and private practice, Totton could still find time to promote the interests of his profession, and did much to improve the status of "chemist" in Northern Ireland. Thus he took an active part in the foundation of the Northern Ireland Section of the Institute of Chemistry and became its first chairman.

His sympathetic nature and sound common sense led his colleagues to seek his advice in their difficulties, and they never sought in vain. In the laboratory he was never ruffled, and he had a charm of manner that endeared him to all with whom he worked. Owing to his official position, he was unable to take any active part in public affairs, although he was prominent in masonic circles, and made very many friends, who found him a delightful companion, and, above all, valued him as one whom they could trust.

Totton was a man who will long be remembered. J. HAWTHORNE

Société de Chimie Industrielle

THE following Address was sent by the Society to the Société de Chimie Industrielle. Dr. L. H. Lampitt acted as representative of the Society and presented the Address.

The President has received from the Société de Chimie Industrielle a letter of thanks, together with a bronze plaque, struck to commemorate the occasion.

FROM
THE SOCIETY OF PUBLIC ANALYSTS
AND
OTHER ANALYTICAL CHEMISTS
TO
SOCIÉTÉ DE CHIMIE INDUSTRIELLE

On the occasion of the Commemoration, in Paris, on September 30th, 1937, of the Twentieth Anniversary of the Foundation of the Société de Chimie Industrielle, The President, Officers, Council and Members of the Society of Public Analysts and Other Analytical Chemists send Fraternal Greetings to the Officers and Members of the Société de Chimie Industrielle.

The Society sincerely welcomes this opportunity to express the friendship and goodwill of its members towards their French confrères and to offer best wishes for the continued prosperity of the Société de Chimie Industrielle.

(*Signed*) G. ROCHE LYNCH (*President*)
E. B. HUGHES (*Honorary Treasurer*)
LEWIS EYNON (*Honorary Secretary*)

Dated this Thirtieth Day of September,
Nineteen Hundred and Thirty Seven

Seal of the Society

Fluorine in Food Products

BY H. C. LOCKWOOD, B.Sc., F.I.C.

(*Read at the Meeting, October* 6, 1937)

THE presence of fluorides in water supplies of certain districts has caused some concern in medical and dental circles. It has been established by Churchill,[1] Smith, Lantz and Smith,[2,3] Ainsworth[4,5] and others, that even minute traces of fluorides produce fluorosis which manifests itself particularly as "mottled teeth" in growing children. The subject of fluorides in food products has received, however, comparatively little attention. Wichmann and Dahle[6] record the following results for produce sprayed with insecticides containing fluorides:—apples, 2 parts per million; cabbage, outside 33·6, inside 2·7; celery (two samples), 7·6 and 3·6 in the petioles, 77·1 and 135·3 in the leaves; preserved strawberry juice, 141 parts per million. Phillips, Hart and Bohstedt[7] found that adding sources of fluorine to cows' diet made no appreciable difference to the fluorine-content of the milk, which normally ranged from 0·05 to 0·25 p.p.m., with an average value of 0·14.

In 1936, Reid[8] published a series of results on Chinese food materials, dealing particularly with tea, in which he found appreciable amounts of fluorine. His results have been converted from parts per 100,000 to parts per million—for ease of comparison with other workers' figures—and are summarised in Table I. Reid used for his determinations Boruff and Abbott's[9] modification of Willard, Arbor and Winter's[10] distillation and titrimetric technique. His results on tea are particularly important, and he considered that the high fluorine-content may be the principal cause of mottled enamel of the teeth among the Chinese. It is interesting to note that foods grown near a fluorite mine show, generally, no increase in fluorine-content.

TABLE I

Material and source	No. of samples	Fluorine (as parts per million) Minimum	Maximum	Average
Chinese tea (various districts)	12	37·5	398·8	109·6
” (fluorite area)	3	15·0	1757·8	614·6
Imported tea	5	8·7	38·1	19·6
Coffee	4	0·2	1·6	0·9
Chinese wine	4	0·05	0·24	0·11
Lemon and orange juice	3	0·14	0·22	0·17
Chinese vegetables	8	1·2	8·5	4·4
Cereals	4	0·2	1·7	1·1
Soya bean	1	—	—	4·0
Foods grown near a fluorite mine—				
Cereals	3	0·2	2·0	1·0
Soya bean	1	—	—	6·7
Miscellaneous	3	1·4	4·3	2·5
Salted and dried mustard leaves	1	—	—	265·5
Salted and dried turnips	1	—	—	40·4

Examination of the foregoing table shows, for solid foodstuffs, figures ranging from 0·2 to 1757·8 p.p.m., which indicate, in my opinion, a greater degree of accuracy than could be attained by the method employed. Calculation shows that to obtain titrimetrically the result of 0·2 p.p.m., a kilogram of material would be required, giving a titration result of 0·5 ml. of 0·02 *N* thorium nitrate, which, considering the indefinite type of end-point, can be regarded as approaching the minimum reliable volume. In view of the statement that the material was ashed with sodium hydroxide, magnesium nitrate and calcium acetate, and the ash distilled with 50 ml. of conc. sulphuric acid, it does not seem likely that much more than 100 g. of a solid foodstuff could have been handled conveniently. My own work indicates that for the above-mentioned volumetric method to be applicable, solid material must contain at least 5 p.p.m. of fluorine.

Although several reactions have been formulated for the detection of traces of fluorine, that originated by de Boer[11] is generally used. He found that a mixture of solutions of zirconium nitrate and alizarin sulphonic acid in the presence of hydrochloric acid was capable of detecting 0·001 mg. of fluorine in 1 ml. of water. The reaction has since been used by Willard, Arbor and Winter[10] as an indicator for the titrimetric determination of fluorine, but the end-point is not very sharp. I have found that by substituting 25 ml. of glycerin for the 25 ml. of ethyl alcohol a decided improvement resulted. Boruff and Abbott[9] used the distillation technique of Willard *et al.*, but made the distillate slightly alkaline and evaporated it to a small volume. Subsequent titration of the concentrated solution would give enhanced accuracy but, as previously stated in connection with Reid's work, with a solid food at least 5 p.p.m. of fluorine must be present. Colorimetric methods based on the fading of de Boer's zirconium-alizarin reagent have been used by Thompson and Taylor,[12] Sanchis,[13] Elvove[14] and Barr and Thorogood[15] for the direct determination of fluorine in water supplies. For the determination of traces of fluorine in foodstuffs I have applied the same principle to the distillate obtained by a modification of the distillation technique of Willard and his collaborators.

EXAMINATION OF A TYPICAL WATER SUPPLY.—As a preliminary investigation I examined the Birmingham water supplied from the Elan Valley. The method of Barr and Thorogood[15] was tried but found inapplicable owing, first, to the small amount of fluoride present and, secondly, to the yellow colour of the residue when the water had been evaporated to concentrate the mineral matter. The distillation technique of Willard, Arbor and Winter[10] was adopted, bumping being prevented by the use of a slow stream of carbon dioxide. A suitable volume (2 litres) was made alkaline, concentrated to a small volume and distilled with perchloric acid. The distillate was tested by the Barr and Thorogood method; in several determinations made during September, 1935, less than 0·1 part per million was recorded.

DISTILLATION OF FLUORINE AS HYDROFLUOSILICIC ACID.—Willard, Arbor and Winter[10] based their method on the distillation of the fluorine as hydrofluosilicic acid by heating the substance with perchloric or sulphuric acid to 135° C., and maintaining this temperature by the steady addition of water until sufficient distillate had been collected. To overcome bumping I used a slow stream of carbon dioxide, but constant attention was still required, and a method of steam-distillation at 135° to 150° C. was therefore devised (*vide infra*).

Mention should be made of the method used by Gilkey, Rohs and Hansen,[16] in which the distillation flask is supported in a vessel containing boiling tetrachloroethane. The steam supply passes through a copper spiral in the vapour, and the superheated steam enters the flask down a glass tube. Owing to the violent oxidation of organic compounds which occurs with perchloric acid above 135° C., it is advocated that sulphuric acid should be used in the flask in case breakage should occur. Although bumping and splashing are prevented, the method is unnecessarily complicated and somewhat inconvenient to use.

FLUORINE IN FOOD PRODUCTS

APPARATUS.—The distillation principle used by Willard and his co-workers was adopted. The apparatus, of the design shown in the diagram (Fig. 1), had ground-glass joints. The distillation tube, 6 in. long and 1¼ in. wide, was fitted with a No. 4 I.S. joint and slightly distended at the closed end. A reducing socket carrying a tube, 0·65 in. internal diameter and 7 or 8 in. long, was attached, together with a still-head having a tubulure through which passed the extended stem of a small tap-funnel. The lower end of the stem was drawn out to a fine capillary, and reached practically to the bottom of the distillation tube. A 200° C. thermometer, having a half-inch bulb, was treated with alcohol and conc. nitric acid to remove the black pigment from the graduation marks, and well washed. The prepared thermometer was attached to the stem of the funnel by means of platinum wire, so that the bulb was level with the end of the capillary

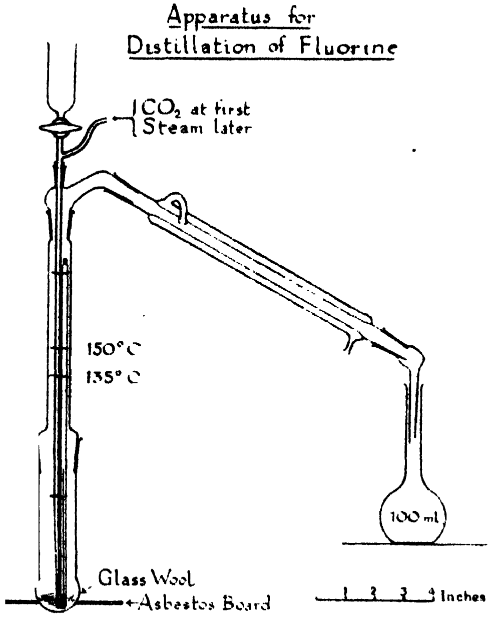

Fig. 1

tube. Owing to difficulty in reading the now faint graduation marks, it was found advantageous to have platinum wire supporting the thermometer at 135° and 150° C. marks, to make these conspicuous. Between the still-head and the funnel-tap a side tube was fitted for connection with a carbon dioxide generator, and later with the steam supply. This tube was suitably inclined to prevent liquid from the funnel flowing the wrong way. The side tube of the still-head was connected with one of the new-type single-surface condensers, having an inner tube with very thin walls for efficient cooling. In the distillation tube the glass beads used by Willard and his collaborators were replaced by a plug of glass wool, which proved more efficacious owing to the relatively greater surface exposed. The distillation tube rested on a piece of asbestos gauze or board, having a hole with a diameter slightly less than that of the tube.

PROCEDURE.—The material was prepared in a moderately fine state of division, and a weighed amount (generally 19 g., which would give direct parts per million) was placed in a platinum dish. Sufficient *N*/10 sodium hydroxide to give an alkaline reaction was added, and the contents of the dish were dried and ashed at a low temperature until ashing was as complete as possible. The dry ash was transferred to the distillation tube, which contained a small quantity of glass wool, and about 15 ml. of water containing a few drops of sulphuric acid were used for removing the residue to the tube from the dish. The apparatus was assembled, 8 to 10 ml. of conc. sulphuric acid were run down the tap-funnel, and the carbon dioxide supply was adjusted to give 3 or 4 small bubbles a second, although until boiling began a faster rate than this was advantageous, since it agitated insoluble matter on the bottom of the tube. The carbon dioxide prevented bumping until a temperature of 135° to 140° C. was attained, at which point the rubber tube was disconnected and replaced by that carrying the steam supply. The flame under the tube was reduced so that the temperature was maintained between 135° and 150° C., and the distillation with steam then proceeded smoothly, occasional adjustment of the burner being required. The distillate was received in a 100-ml. graduated flask, and afterwards a further 50 ml. were collected in a Nessler cylinder to ascertain if all the fluorine had distilled. The distillation of 150 ml. generally took about 45 minutes, and there was no trouble with bumping.

THE EFFECT OF CHLORINE IN THE DISTILLATE AND ITS ELIMINATION.—In tests on some ginger biscuits it was found that appreciable amounts of fluorine appeared to be present. This was proved to be due to traces of manganese, a natural constituent of powdered ginger. On ashing in the presence of sodium hydroxide a certain amount of permanganate was formed which, when heated with sulphuric acid, liberated chlorine from chlorides present. The distillate from powdered ginger caused the zirconium–alizarin indicator to fade rapidly, and gave a reading equivalent to 700 parts of fluorine, though later it was shown that only 1 part per million was present. Although the distillate from ginger made the indicator fade, yet, when the volumetric method of Willard[10] was tried, the colour of the indicator would not return to give the required end-point. In order to remove the chlorine without adversely affecting the zirconium–alizarin indicator, a number of substances were tried. The most satisfactory of these was sodium nitrite, which in half-an-hour removes every trace of chlorine.

As one would expect, other foodstuffs containing manganese are liable to behave in the same way as ginger. This has been confirmed with tea, a commodity in which Reid[8] reported very appreciable amounts of fluorine when using the titrimetric technique. Bodenstein[17] reported the presence of traces of manganese in pineapple, but in the sample of tinned pineapple that I examined no permanganate was formed on ashing, and the material was also free from fluorine.

Owing to the effect of free chlorine on the zirconium–alizarin reagent, it is evident that the technique of Barr and Thorogood[15] is somewhat inadequate, as in some districts appreciable amounts of chlorine are used in the purification of water supplies. Moreover, as conc. hydrochloric acid after storage is liable to contain traces of chlorine, it recommended that the Barr and Thorogood procedure for fluorine in water should be modified by including a treatment with sodium nitrite.

PREPARATION OF THE ZIRCONIUM–ALIZARIN REAGENT.—The indicator was prepared as described by Willard *et al.*,[10] the following solutions being used:—(*a*) 0·4 per cent. zirconium nitrate, (*b*) 1 g. of sodium alizarin sulphonate dissolved in 100 ml. of ethyl alcohol, and the solution filtered and made up to 250 ml. with alcohol. For use, 3 volumes of (*a*) were mixed with 2 volumes of (*b*) and diluted to 10 times the volume with water. The mixed indicator is serviceable for a week, after which a fresh supply should be prepared.

The solution thus prepared was preferred to that of Barr and Thorogood,[15] since it gives a brighter and more intense colour. The addition of hydrochloric acid which they recommended was found to be essential for making the reaction sensitive, and the optimum concentration was 2 ml. of the concentrated acid in 50 ml. of the test solution.

METHOD OF DETERMINATION.—Instead of preparing a number of standard tubes each time, as in Barr and Thorogood's method, it was found simpler and decidedly more effective to compare the fading produced by aliquot parts of the distillate with that in a tube containing a definite amount of fluoride and indicator. The standard fading test solution was therefore prepared with 10 ml. of 0·0001 *N* lithium fluoride, obtained, as required, by suitably diluting a 0·02 *N* solution. The lithium fluoride solution was pipetted into a Nessler tube, and 40 ml. of water, 2 ml. of conc. hydrochloric acid and 1 ml. of 10 per cent. sodium nitrite solution were added. The contents were well mixed and allowed to stand half-an-hour. A "blank" standard was also prepared with 50 ml. of water and the above-mentioned quantities of reagents. The preliminary testing of the first 100 ml. of distillate was generally carried out by treating 50 ml. in a manner identical with, and at the same time as, the standard fading test and blank solutions.

After half-an-hour any nitrous fumes in the upper parts of the cylinders were removed by means of a current of air, 1·5 ml. of the dilute zirconium–alizarin reagent was added to each, and the liquids were well mixed. The degree of fading was noted at intervals of approximately 30 minutes over a period of 2 hours or longer. It was quite practicable, and for the final matching preferable, to allow the fading to continue overnight, as judging in daylight was easier than by artificial illumination. The contents of the standard "fading" tube were of such composition that the slightest indication of pink persisted for several hours; this condition is considered optimum for comparison. If preferred, a tube containing half the standard amount of fluorine can also be prepared, but generally this was not considered necessary.

As a rule, the first series of tests gave a good idea of the range required, so that for the final matching suitable volumes of distillate could be chosen accordingly and treated as described above; a standard "blank" and a standard "fading" tube for comparison were always prepared. The tube containing the 50 ml. of distillate collected after the first 100 ml. was tested at the same time, but never caused the indicator to fade to the extent of more than half the standard, except with tea containing appreciable amounts of fluorine. When dealing with materials having a fluorine-content of 1 part per million or less, it was necessary to concentrate the first 150 to 200 ml. of distillate to about 40 ml. after it had been made slightly alkaline with sodium hydroxide. The solution was then transferred to a Nessler tube, made up to 50 ml., and tested as prescribed; the estimation was made to 0·5 part per million.

Assuming that 19 g. of material were originally taken, the fluorine, as parts per million, equals the volume of distillate, *i.e.* 100 ml., divided by the volume of distillate required to fade the same amount as the standard tube. If the final 50 ml. showed half fading, 0·5 part per million was added to the result.

RECOVERY OF ADDED FLUORINE.—Consideration of the results given in Table II shows a fairly satisfactory recovery of added fluorine from several foodstuffs. The low result with biscuits was probably due to incomplete ashing of the material. The accuracy with which solutions can be matched diminishes with the increase in fluorine-content; at 5 parts per million and upwards the titrimetric method should be applied to the concentrated distillate.

TABLE II

RECOVERY OF ADDED FLUORINE (AS PARTS PER MILLION)

Material	Fluorine added	Total fluorine indicated	Added fluorine recovered
Water	nil	nil	—
	4	4	4
Cocoa	nil	2	—
	5	7	5
Biscuits	nil	nil	—
	5	4	4
Milk chocolate	nil	2	—
	5	6·5	4·5
Beef	nil	2	—
	3	4·5	2·5

FLUORINE IN SOME FOOD PRODUCTS.—The investigation was intended primarily for confectionery materials, but general foodstuffs have been included for comparison, and the results are given in Table III. It will be noticed that, with the exception of the five teas examined, the fluorine-content did not exceed 2 parts per million. It is generally recognised that fluorine in excess of 1·5 p.p.m. in water

constitutes a danger to health, but it may be suggested that foodstuffs may contain appreciably more than this before being regarded as unfit for human consumption.

TABLE III

FLUORINE IN FOOD PRODUCTS

Material	Fluorine (as parts per million)
Biscuit flour	nil
Gelatin	nil
Pineapple (tinned)	nil
Glucose	0·5
Plain chocolate	0·5
White bread	1
Potato	1
Honey	1
Powdered ginger	1
Malt (2 samples)	1, 1·5
Cocoa (3 samples)	0·5, 0·5, 2
Milk chocolate (3 samples)	0·5, 1, 2
Biscuits (5 samples)	nil, nil, 1, 2, 2
Ginger biscuits (3 samples)	2, 2, 2
Egg yolk	2
Beef	2

FLUORINE IN TEA.—Reid recorded the presence of 8·7 to 1757·8 p.p.m. of fluorine in the teas he examined, and found that 2 per cent. infusions after 5 minutes contained in solution 82 to 97 per cent. of the total fluorine. I have examined five teas, 300 to 400 ml. of distillate being collected in each instance, and the results are given in Table IV. With samples 3 and 5, 2·5 per cent. infusions were prepared and allowed to stand, with occasional mixing, for 5 minutes. The aqueous part was decanted and the residue was drained for half-a-minute. No further water was added, the object being to find the proportion which would be dissolved in normal practice. The results in Table IV show this to be approximately 75 per cent. of the total fluorine. Eight per cent. of the added water remained in the wet leaves, and calculation shows that with the China and Indian teas examined, 81 and 82 per cent. respectively of the total fluorine was in solution. The amounts of fluorine in the tea infusions and the residual leaves, determined for samples (3) and (5), agree well with the total amounts found in the teas directly.

TABLE IV

Material	Fluorine (as parts per million)	Dissolved in 2·5 per cent. infusion	Remaining in leaves
(1) Fine leaf tea	10	—	—
(2) China tea, A	40	—	—
(3) China tea, B	47	35	12
(4) Indian tea, A	60	—	—
(5) Indian tea, B	70 73 (by titrimetric method)	53	18

FLUORINE IN CHEMICAL INGREDIENTS.—As a matter of some importance, a number of chemical substances which may be used in connection with foodstuffs, *e.g.* baking powder, or in fireproofing material, were examined. The distillation method was not applicable to chlorides and was not used for carbonates. Solutions were prepared and filtered, before use, through well-washed filter-papers. Aliquot parts were then tested until a known amount faded to the same extent as the standard tube containing 10 ml. of 0·0001 *N* lithium fluoride solution. For carbonates, sufficient hydrochloric acid was added to neutralise the solution, followed by 2 ml. required for the test. Phosphates were distilled with sulphuric acid, and the distillate was concentrated and re-distilled with perchloric acid, as recommended by Churchill, Bridges and Rowley.[18] The results, given in Table V, range from 1 to 16 p.p.m.

TABLE V

Chemical substance	Fluorine (as parts per million)
Sodium chloride (*a*)	6
" (*b*)	6
Sodium carbonate (*a*)	3
" (*b*)	2
Sodium bicarbonate	1
Ammonium carbonate	3
Sodium di-hydrogen phosphate	6
Di-sodium hydrogen phosphate ($12H_2O$) ..	5
Ammonium phosphate	16

SUMMARY.—(1) The fluorine is steam-distilled at 135° to 150° C. in an apparatus of special design having ground-glass joints and containing glass wool and sulphuric acid; a slow stream of carbon dioxide is used to prevent bumping until a temperature of 140° C. has been attained. Distillation is complete in 45 minutes, and the fluorine-content is determined by "fading" zirconium-alizarin reagent in a similar way to that described by Barr and Thorogood.[16]

(2) The use of sodium nitrite is recommended for nullifying the bleaching effect of free chlorine, which is liable to be obtained with foodstuffs containing manganese, owing to the formation of permanganate on ashing.

(3) The volumetric method of Willard *et al.*[10] is discussed; it was found suitable for foodstuffs containing more than 5 p.p.m. of fluorine, but the use of 25 ml. of glycerin gave a much better end-point than 25 ml. of ethyl alcohol.

(4) Results are given showing that a satisfactory recovery of added fluorine is obtained by the method referred to in (1) and (2); the fluorine-contents of 17 different foodstuffs and 7 chemical substances are recorded.

(5) The fluorine-content of the foodstuffs examined did not, as a rule, exceed 2 p.p.m., but the important observation of Reid,[8] that tea contains considerably larger amounts of fluorine, is confirmed.

I wish to thank Mr. A. W. Knapp and Mr. J. R. Johnson for their interest and advice, and Messrs. Cadbury Brothers, Ltd., for permission to publish this work, which was carried out in their laboratories at Bournville.

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CHEMISTS' DEPARTMENT
BOURNVILLE
BIRMINGHAM

DISCUSSION

The PRESIDENT remarked that in considering the possible toxic effects of fluorine it was important to distinguish between fluorine present in soluble and insoluble forms. The latter, even if in suspension in infusions, might not have any toxic effect.

Mr. R. W. SUTTON said that, in view of the occurrence of fluorspar in parts of Derbyshire, he had examined 30 to 40 water supplies in that district, using the method of Sanchis; in only one of the waters did he find more than one part per million.

Dr. B. S. EVANS, referring to the state of solubility of the fluorine, remarked that in teas, for example, it might possibly be in a colloidal state.

Mr. A. L. BACHARACH pointed out that many "toxic" substances (copper, for example) were harmless or even essential in minute quantities. It was therefore incorrect to speak of a substance as toxic or innocuous without reference to its concentration. It was not known at present if minute traces of fluorine were beneficial or at what concentration it became definitely injurious, and he welcomed the paper because the method described seemed to provide a means of obtaining light on these matters.

Mr. E. R. BOLTON recalled a time when relatively very large quantities of fluorine in foodstuffs were tolerated, and even thought by some to be beneficial.

Mr. E. HINKS also recalled an instance, years ago, of a food manufacturer advertising a product as bone-building on account of its fluorine-content.

Mr. C. E. SAGE asked if special precautions had been taken to eliminate the possibility of manganese causing high results. Was it only a coincidence that both tea and Cochin ginger, which contained notable amounts of manganese, gave such high figures for fluorine by the author's method?

Mr. LOCKWOOD, replying to questions in the discussion, said that numerous blank determinations had been carried out with the apparatus, but on no occasion was the presence of fluorine indicated, showing that the fluorine did not result from fluorides in the glass or reagents. This was supported by the number of commodities in which no fluorine was detected—water, biscuit flour, biscuits, gelatin and pineapple. With regard to the solubility of the fluorine in tea, he laid stress upon the fact that the decanted liquid was clear and bright while hot, and the extracted fluorine was presumably in solution. In any event, a high proportion of the fluorine present was imbibed and was liable to be in a condition for ready absorption. The reason why more people did not suffer from mottled teeth was owing to the effect being generally restricted to growing children, who normally had very weak tea, the fluorine-content of which would not reach the danger mark of 1 part per million. In the United States of America it was proposed to fix a maximum limit of 1·4 part per million in foodstuffs. In reply to Mr. Sage, the author remarked that there seemed to be no connection between manganese-content and the amount of fluorine present; tea contained significant amounts of fluorine, whilst the powdered ginger examined contained only 1 part per million. In the presence of manganese, however, it was necessary to avoid the effect of free chlorine in the analysis; this was done by the addition of nitrite, as explained in the paper.

Characteristics of Some Reputed Cod-Liver Oils

By R. H. COMMON, B.Sc., Ph.D., A.I.C.

During December, 1936, and January and February, 1937, fourteen samples of "cod-liver oil," as sold for stock-feeding, were purchased in various towns in Northern Ireland, and subsequently examined in this laboratory. One suspicious sample (No. 5), one reliable guaranteed medicinal cod-liver oil (No. 16), and two reputable guaranteed stock-feeding cod-liver oils (Nos. 17 and 18) were also examined.

Unsaponifiable matter was determined by the ether extraction method of Archbutt and Deeley (*Lubrication and Lubricants*, 1926), the iodine value of the unsaponifiable matter by the method of Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154; Analyst, 1924, **49**, 105), and the blue value on the lines of the B.P. 1932 method. Other characteristics were determined by the usual standard methods.

The presence of mineral oil is readily detected by intense bright blue fluorescence under the quartz mercury vapour lamp. Sperm oil gives a greenish-blue fluorescence, but this is masked by the bright grass-green fluorescence of shark-liver oil or cod-liver oil unless more than about 50 per cent. of sperm oil is present.

When the presence of shark-liver oil was suspected, 100 ml. of the oil was distilled *in vacuo* (3 to 4 mm. mercury), and the distillate was collected up to about 260° C. The distillate was dissolved in cold dry acetone saturated with hydrogen chloride, and dry hydrogen chloride was passed into the solution (Heilbron, Kamm and Owens, *J. Chem. Soc.*, 1926, 1630). The presence of the characteristic crystals of squalene hydrochloride after the solution had been in the refrigerator overnight formed a useful qualitative test for shark-liver oils of the squalene-containing group (Tsujimoto, *J. Soc. Chem. Ind.*, 1932, **51**, 317T).

The results of the examinations are summarised in the accompanying table. The medicinal cod-liver oil (No. 16) and the two guaranteed cod-liver oils (Nos. 17 and 18) had the characteristics of good cod-liver oil. No. 8 had the characteristics of cod-liver oil, although the iodine value of the unsaponifiable matter

TABLE I

CHARACTERISTICS OF REPUTED COD-LIVER OILS

Oil No.	Sp.gr. (15·5°/15·5° C.)	n_D^{40}	Free fatty acids (as oleic acid) Per Cent.	Saponification value	Iodine value (Wijs)	Blue value	Unsaponifiable matter Per Cent.	Iodine value of unsaponifiable matter	Nature of unsaponifiable matter	Fluorescence of oil in ultra-violet light
1	0·920	1·4673	0·54	177	139	13·5	10·4	145	Viscid pale yellow oil	Bright grass-green
2	0·916	1·4687	0·14	149	118	36·8	18·3	70	Greenish fatty solid	„ „
3	0·914	1·4688	0·28	149	119	34·5	19·6	70	„ „ „	„ „
4	0·917	1·4689	0·42	153	121	27·2	18·4	65	„ „ „	Bright grass-green, trace blue-green
5	0·908	1·4751	0·48	98	102	(0·7?)	51·0	10	Mobile pale oil	Intense bright blue
6	0·924	1·4684	0·71	186	140	nil	1·77	65	Viscid oil with small crystals	Bright grass-green
7	0·933	1·4730	0·65	192	182	1·5	0·83	63	Viscid pale yellow oil	Livid blue-green
8	0·928	1·4714	0·48	187	162	14·8	1·11	72	Yellow semi-crystalline solid	Grass-green, trace blue-green
9	0·899	1·4696	0·42	104	97	nil	44·1	20	Mobile pale oil	Intense bright blue
10	0·918	1·4694	0·71	163	146	29·6	9·1	278	Greenish fatty solid	Bright grass-green
11	0·919	1·4680	0·48	175	144	13·6	9·75	170	Very viscid pale yellow oil	„ „
12	0·925	1·4678	1·40	188	147	5·6	0·93	92	Yellowish solid	„ „
13	0·928	1·4713	0·73	188	167	3·6	1·62	70	„ oil	Blue-green
14	0·918	1·4683	0·22	163	130	22·0	11·6	93	Greenish fatty solid	Bright grass-green
15	0·914	1·4718	0·45	134	116	3·1	25·9	19	Mobile pale yellow oil	Intense bright blue
16	0·927	1·4708	0·48	186	162	14·4	1·37	—	Viscid yellow oil	Bright grass-green
17	0·927	1·4720	0·45	190	162	10·4	1·15	117	Yellow semi-crystalline solid	„ „
18	0·926	1·4711	0·25	176	162	12·4	0·96	108	Yellow semi-crystalline solid	„ „

was rather low and the fluorescence slightly different from that of good cod-liver oil. No. 12 was apparently a rather poor sample of cod-liver oil, and No. 18 had, in the main, the characteristics of cod-liver oil, but the low iodine value of the unsaponifiable matter and the blue-green fluorescence were unsatisfactory features.

Nos. 5, 9 and 15 contained varying proportions of mineral oil. Nos. 2, 3, 4 and 14 were apparently mixtures of sperm oil with shark-liver oil, and Nos. 3, 4 and 14 gave small but definite yields of squalene hydrochloride. Nos. 1, 10 and 11 were apparently shark-liver oils, and gave significant yields of squalene hydrochloride (No. 11 gave a large yield). No. 6 gave Hoppenstedt's colour reaction for menhaden oil (*J. Soc. Chem. Ind.*, 1911, 30, 36T) very strongly, none of the other oils responding to this test. No. 7 was not identified, but it does not appear to be cod-liver oil.

The results of the examination suggest that a fairly varied assortment of marine oils is still being offered for sale as cod-liver oils for stock-feeding.

Chemical Research Division
Ministry of Agriculture for Northern Ireland
Belfast

The Use of Selenium in the Determination of Nitrogen in Potato Tubers

By A. M. SMITH, Ph.D., D.Sc., A.I.C., and W. Y. PATERSON, B.Sc.

(*Read at the Meeting of the Scottish Section, April* 16, 1937)

Since Lauro[1] drew attention to the value of selenium as a catalyst in the Kjeldahl digestion of cereal products, several investigations have been carried out to compare selenium, alone or mixed with compounds of mercury or copper, with the catalysts commonly used. In most instances the results have shown that with selenium a much shorter time suffices to obtain maximum figures for the nitrogen in various organic substances. Thus, Ashton[2] found that selenium was more efficient, in the analysis of grass, than copper sulphate in curtailing the time of heating by about 90 minutes, whilst Beet and Furzey,[3] using a mixture of selenium and mercuric sulphate, obtained, in the examination of various foodstuffs, maximum nitrogen results after 16 to 23 minutes' heating, or about one third of the time required by the method recommended in the Fertilisers and Feeding Stuffs Regulations.

There is, however, a considerable lack of agreement among the observations and conclusions of different investigators as to experimental details. It is generally accepted that digestion is not necessarily complete when the liquid has become clear, and that a further period of heating ("after-boil") is essential to complete the reaction. It is also obvious that the time of heating required depends on the composition of the catalyst mixture. Illarionow and Ssolowjewa[4] have examined the mechanism of the reaction, and point out that the selenium is oxidised to selenious acid, which is the actual catalyst concerned, and that, although the catalytic effect is proportional to the amount of catalyst present when the amount is small, excess of selenium or prolonged heating leads to a loss of nitrogen, probably as a result of the decomposition of ammonium selenite with liberation of free nitrogen. In short, it would seem to be impossible to define the best conditions for the decomposition of a substance without a study of the reaction in question.

In the course of an investigation of the nitrogen in potato tubers, which do not appear to have been included in other investigations on foodstuffs, it was felt that a considerable saving of time in the digestion might result from using selenium instead of copper sulphate, and the following data were collected in the preliminary study of methods. A number of tubers, variety Majestic, were dried at 90° C. and ground up to supply material for examination, 1 g. being used for each determination. In order to determine the effect of "after-boil" on the results, a mixture containing 9·7 g. of potassium sulphate and 0·3 g. of selenium was added, together with 25 ml. of sulphuric acid. The heating was carried out in 500-ml. flasks over a series of Bunsen burners, and the arrangement of flasks and Bunsens was quite a random one. After digestion, the liquid was transferred to a distilling flask and made alkaline with caustic soda, and the ammonia was distilled into standard acid. The average figures from quadruplicate determinations are given in Table I.

TABLE I

EFFECT OF PERIOD OF "AFTER-BOIL" ON THE PERCENTAGE OF NITROGEN

Time of "after-boil" in min.	0	10	30	60	120
Mean per cent. of nitrogen ..	1·008	1·100	1·110	1·108	1·113
Standard error	0·005	0·008	0·007	0·008	0·012

The results agree with those obtained by Beet and Furzey, and it was decided that heating for 20 minutes after the liquid became clear was adequate in this instance, which meant that the digestion was complete in about 30 minutes. When 0·3 g. of copper sulphate was used instead of selenium, the liquid became clear after 35 to 40 minutes, and a subsequent heating of about 30 minutes was required to get maximum figures for nitrogen.

TABLE II

EFFECT OF DIFFERENT AMOUNTS OF SELENIUM ON PERCENTAGE OF NITROGEN

Weight of selenium in g. ..	0·15	0·30	0·45	0·70	1·00
Mean per cent. of nitrogen ..	1·048	1·100	1·023	0·950	0·950
Standard error	0·011	0·008	0·013	0·016	0·011

The effect of varying the amount of selenium in 10 g. of the catalyst mixture was also examined, the time of heating in each instance being 20 minutes after the solution had cleared. The results (Table II) indicate that the amount of selenium used is of considerable importance, and that, under the experimental conditions described, 0·3 g. is the most suitable quantity to take. This amount is of the same order as the amounts used by Beet and Furzey and by Ashton, but is nearly four times as much as that recommended by Illarionow and Ssolowjewa. The last-mentioned chemists, however, worked with a simple organic compound, aniline sulphate, and used only 5 g. of potassium sulphate in each digestion.

The low results with the larger quantities of selenium, recorded in Table II, confirm those of other observers who found that large doses of the catalyst had this effect.

A further series of determinations, made on dried material and directly on fresh material from a single tuber, gave average results of 1·47 and 1·51 per cent. of nitrogen respectively, both calculated on the dry material; it is not known whether the discrepancy was due to the preliminary preparation of the dried samples or to the dilution of the digestion mixture by the 80 per cent. of water in the fresh samples.

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EDINBURGH AND EAST OF SCOTLAND COLLEGE OF AGRICULTURE

The Rapid Determination of Copper in Mild Steel

BY T. P. HOAR, M.A., PH.D., B.SC.

THE small amounts of copper found in mild steel may be rapidly and accurately determined colorimetrically by means of sodium diethyldithiocarbamate. The steel is taken up in dilute sulphuric acid, which leaves a residue containing almost all the copper, as noted by Reinhardt,[1] Koch[2] and Zinberg[3]; a little iron also remains undissolved, probably as carbide. The trace of dissolved copper is precipitated by addition of copper-free zinc, as suggested by Mohr[4] and others; Price[5] and Koepping[6] prefer aluminium for this purpose. The whole residue is then taken up in nitric acid. After suitable dilution, the copper is determined colorimetrically in the presence of the small remaining amounts of iron and zinc by the modified sodium diethyldithiocarbamate method previously described.[7]

The advantages of the method are:

(1) The main separation is effected by the initial process of solution; the precipitation of the trace of dissolved copper by zinc rather than by hydrogen sulphide avoids loss of copper (due to oxidation or peptisation of sulphide) during filtration.

(2) The colorimetric method using sodium diethyldithiocarbamate is at least as accurate as the electrolytic for such small amounts of copper, unless very special apparatus is available, and is very much quicker. It is much better than the iodimetric method, which requires either the removal of the small amount of iron still present as hydroxide, or the addition of fluoride, neither of which procedures is very suitable when very small amounts of copper are involved.

REAGENTS REQUIRED.—(i) Sulphuric acid: about 250 g. per litre (1 vol. of conc. sulphuric acid to 7 vols. of water); (ii) copper-free zinc (thin foil or filings); (iii) conc. nitric acid and the reagents listed in the preceding paper.[7]

PROCEDURE.—Dissolve 5 g. of steel in 80 ml. of sulphuric acid (250 g. per litre) in a 150-ml. beaker on the hot-plate until evolution of gas ceases (about 40 minutes). Dilute to 150 ml. and add 1 g. of copper-free zinc, stirring until it has almost all dissolved (5 minutes). Filter through a Gooch crucible or coarse glass frit fitted with one layer of filter-paper only (for rapidity, to avoid oxidation), wash the residue once with cold water and return it, with the filter-paper, to the beaker. Add 3 ml. of conc. nitric acid and return the beaker to the hot-plate. When the particles *in* the small filter-paper have dissolved (5 minutes), remove the paper, washing it well. Heat until the solution has a clear brown colour; a small brownish residue (probably SiO_2 and SnO_2) may be neglected. Add 0·5 g. of urea and boil for 2 minutes, to remove nitrous acid. Cool and make up to 200 ml. Take two 10-ml. or other convenient aliquot portions, and determine the copper by the citrate method of the preceding paper.[7]

Use half quantities if desired, making the solution up to 100 ml. Make a blank test to determine any traces of copper in the acids or the zinc. No filtration is necessary; add the nitric acid after the zinc has dissolved in the sulphuric acid. Add a considerable amount of ammonia or some sodium hydroxide to keep the zinc in solution.

Where the greatest accuracy is not essential, but rapidity is desired, omit the addition of zinc, and determine the copper by the pyrophosphate method of the preceding paper.[7]

TEST OF THE METHOD.—It was necessary to show that the residue after the zinc treatment contains all the copper originally present in the steel. The middle part of a sheet of dead-mild steel of the tinplate type was carefully cleaned with emery-paper and cut into small pieces, about 0·5 by 0·5 cm., which were thoroughly mixed. Copper was determined in 5-g. samples of this uniform material by the method as described. Precipitation by hydrogen sulphide or sodium thiosulphate, and determinations without precipitation, were also tried. In each instance the copper in the filtrate was determined by the method of Haddock and Evers,[8] the large excess of ferrous iron being oxidised with nitric acid and fixed with the appropriate excess of citric acid. The results are shown in Table I.

TABLE I

Steel taken g.	Precipitation method	Copper found in residue mg.	Copper found in filtrate mg.	Copper found (residue only) Per Cent.	Copper found (total) Per Cent.
5·02	Zinc	5·4	0·00	0·107	0·107
5·00	"	5·3	0·04	0·106	0·107
5·00	"	5·3	0·00	0·106	0·106
5·02	H_2S	5·2	0·06	0·104	0·105
5·00	"	5·2_5	0·14	0·105	0·108
5·01	Thiosulphate	5·2	0·16	0·104	0·107
5·03	"	5·2	0·09	0·103	0·105
5·03	None	5·2_5	0·13	0·104	0·107
5·02	"	5·2	0·09	0·104	0·105

Clearly the zinc precipitation is effective, whilst the sulphide precipitations offer no advantage over the omission of the precipitation altogether. Results obtained without the zinc precipitation may be expected to be systematically about 2 to 3 per cent. low.

The small amount of zinc which may be present if the liquid is filtered before the added zinc has entirely dissolved has no ill effect; any turbidity produced can be eliminated by making the solution more strongly ammoniacal.

To confirm the conclusion previously reached,[7] that the nitric acid used to take up the copper has no influence on the copper determination, several analyses of the steel referred to above were made, with and without the removal of excess nitric acid, by "fuming" with sulphuric acid, by the method previously described[7] without the zinc addition. The results were as follows (Table II):

TABLE II

Procedure	Nitric acid removed				Nitric acid not removed				
Copper found, per cent.	0·103	0·104	0·104	0·103	0·103	0·104	0·102	0·104	0·104

Evidently the nitric acid has no influence.

The only other ion likely to be present is a trace of arsenate derived from arsenic in the steel. As noted in the preceding paper,[7] this does not interfere.

This work, and that of the preceding paper, has been carried out for the International Tin Research and Development Council in connection with investigations of the steel-base of tinplate.

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THE METALLURGICAL LABORATORIES
UNIVERSITY OF CAMBRIDGE

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF TOTAL ALKALOIDS IN COCOA, AND OF COCOA-MATTER IN FLOUR CONFECTIONERY

THE useful method of determining the total alkaloids, published by Moir and Hinks (ANALYST, 1935, **60**, 439), is tedious, owing to the low solubility of theobromine in chloroform. As stated, ten to twelve extractions of the final solution by chloroform may be necessary to ensure complete removal of the alkaloids, otherwise the results are uncertain.

In an endeavour to shorten and improve this part of the process, the use of several other solvents was tried, and one of them—chloroform and phenol, as recommended by Autenrieth (*Detection of Poisons*, 6th Ed., p. 624)—was found to give the best results. Chloroform and alcohol, as recommended by Nicholls (ANALYST, 1922, **47**, 506), for the extraction of morphia was also tried, but the results were not so satisfactory.

The following table gives the results, in grams, obtained by the use of various solvents. An aqueous solution containing 0·025 g. of theobromine was extracted four times with 40 ml., 30 ml., 20 ml. and 10 ml. respectively of the solvent:

	Chloroform plus phenol				Chloroform plus alcohol (50/50)
Chloroform	1%	2%	5%	10%	
g.	g.	g.	g.	g.	g.
0·008	0·012	0·015	0·025	0·025	0·015

A 5 per cent. solution of phenol in chloroform was afterwards adopted as the best solvent for the purpose.

The final solution of alkaloids obtained from a sample of chocolate cake by Moir and Hinks's method yielded 0·013 g. of mixed alkaloids to chloroform after 12 extractions, and 0·018 g. to a 5 per cent. solution of phenol in chloroform after 4 extractions, as previously detailed. The extracts may contain a trace of sugar, and their nitrogen-content should be determined.

It was found by experiment that 100 ml. of a solution of 5 per cent. of phenol in chloroform would, in 24 hours at ordinary temperature, take up 0·23 g. of pure theobromine, whilst 100 ml. of chloroform would take up 0·03 g., and 100 ml. of equal parts of chloroform and alcohol 0·11 g.

When a mixture of phenol and chloroform is distilled on a water-bath, the phenol is left behind; it can be removed conveniently by holding the flask in the fingers and rotating it over a small flame while sucking a gentle current of air through it with a filter-pump.

An alternative procedure recommended is the extraction of the final solution with chloroform in a Pregl type of extractor (Autenrieth, p. 467). In 9 hours, 0·024 g. of theobromine was extracted from a solution containing 0·025 g.

ALBERT E. PARKES
HUBERT A. PARKES

161, BOW ROAD
LONDON, E.3

IODINE VALUE OF SHELLAC

An important investigation into the various factors affecting the iodine value of shellac, as determined by the Wijs–Langmuir method, was made by a Sub-Committee on Shellac Analysis of the Committee on Uniformity in Technical Analysis (*J. Amer. Chem. Soc.*, **1907, 29, 1221**). One of the most significant points established was the comparatively large effect of variation in the concentration of the acetic acid used in the test. This is shown by the results in the following table:

Strength of acetic acid Per Cent. (approx.)	Melting-point of acid	Iodine value
97	11·8° C.	14·67
99	14·95° C.	17·59
100	16·4° C.	20·48

These results have been confirmed in general by a number of research laboratories, including those of Messrs. Angelo Bros., Calcutta, the Indian Lac Research Institute, and the London Shellac Research Bureau.

Unfortunately, the details of the Wijs method for the determination of the iodine value of oils and resins given in various publications in this country (*e.g. Analysis of Resins*, by K. Dieterich, and *Oil and Colour Chemists' Handbook*) specify *glacial* acetic acid, without qualification as to strength and, thus, such specifications are unsuitable for shellac analysis. A specification (*A.S.T.M.*, 1930, p. 299), which has been found to give every satisfaction, aims at overcoming this difficulty by prescribing "glacial acetic acid, 99 per cent., having a melting point of 14·8° Centigrade and free from reducing impurities. If these requirements are not complied with, the result of the iodine number determination will be erratic."

In view of the fact that certain consumers of shellac have obtained high iodine values by using *glacial* acetic acid without dilution, it was felt advisable to draw attention to the earlier work on this test.

R. W. Aldis

London Shellac Research Bureau
India House
Aldwych, London, W.C.2

Official Appointments

The Minister of Health has approved the following appointments:

Samuel Russell Trotman as a Public Analyst for the County Borough of Nottingham, in addition to William Wilder Taylor (May 28th, 1937).

Note:—Mr. S. R. Trotman retired on December 31st, 1936, on the appointment of Mr. W. W. Taylor as Public Analyst. The appointment of an Additional Public Analyst has become necessary owing to Mr. Taylor being away from business on account of illness.

Harold Edward Monk as a Public Analyst for Borough of Kidderminster, in place of C. C. Duncan, retired (June 10th, 1937).

Rhys Pendrill Charles as a Public Analyst for the Borough of Penzance, in place of W. Partridge (deceased) and in addition to C. G. Moor (June 16th, 1937).

Frederick Grant Duncan Chalmers as a Public Analyst for the County Borough of West Bromwich, from July 1st, 1937, in place of Harry Silvester, resigned June 30th, 1937 (September 10th, 1937).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

METROPOLITAN BOROUGH OF STEPNEY

ANNUAL REPORT OF THE BOROUGH ANALYST

OF the 1575 samples of food and drugs examined, 1025 were taken formally and 550 informally.

DETERMINATION OF HORTVET FIGURE BY ASSISTANT.—In one case objections were raised by the defence because the determination of the freezing-point had not been made by the Public Analyst himself. This involved the appearance of both my assistant and myself to give evidence. In the case of *Bakewell* v. *Davis*, 1894, in which the analysis had been done by an assistant under the supervision of the Public Analyst, the judges were of opinion that the Public Analyst had analysed the sample within the meaning of the Act (*cf.* ANALYST, 1881, **6**, 152; 1888, **13**, 143; 1930, **55**, 39).

SODA WATER.—Three samples of soda water were analysed. Two of these contained 7·3 and 8·1 grains of sodium bicarbonate per pint respectively; the remaining sample consisted of aerated tap water. There is no definite standard for sodium bicarbonate in soda water. It is generally admitted that a reasonable standard is 10 grains of sodium bicarbonate per pint of soda water, and many mineral water manufacturers conform fairly closely to that standard, the sodium bicarbonate varying from 5 to 10 grains per pint. The soda-free article is usually cheap and probably satisfies many purchasers, but it should be labelled "Aerated water," or the absence of sodium bicarbonate should be declared.

DOUGLAS HENVILLE

Department of Scientific and Industrial Research

REPORT OF THE BUILDING RESEARCH BOARD FOR THE YEAR 1936*

THE Annual Report of the Building Research Board for 1936 contains a survey by Dr. R. E. Stradling of the work of the Building Research Station since its establishment eleven years ago. It is mentioned *inter alia* that one investigation is likely to lead to specification testing of cement being placed upon a new footing, and that in another, methods have been evolved by which the variations in concrete, as produced on a job, can be reduced. Chemical studies have led to the discovery of substances from British sources which render concrete more resistant to chemical attack. The work has also resulted in new industries being started. For instance, the production of bricks by a steam-curing process from spent oil shale and lime has been investigated, and the commercial production of this type of brick has been started in Scotland. Commercial production of materials for making good light-weight concrete from blast-furnace slags has also been begun.

Studies have been made of the properties of building stones and the causes of their weathering and decay, and attention has also been devoted to the properties of bricks.

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* **H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 4s. net.**

It is now possible to examine samples of clay and indicate the best firing temperature for bricks made from it. It is also possible to estimate the risks involved if this temperature is not obtained. The importance of particular firing temperatures in eliminating the salts which by crystallising out may cause unsightly stains or even the disintegration of bricks has been clearly shown.

The work on plaster mortars and rendering has shown that the weaker porous mortars are more efficient in preventing damp penetrating into walls than the more impermeable cement renderings, since the shrinking of the latter causes cracks to form.

CLEANING BUILDINGS.—The work of the past year has shown that plain water is the most efficient cleaning agent. It has been found that by directing a fine spray of water on to the surface for a period depending on the nature and condition of the stone, the soot incrustations become so thoroughly softened that they can often be brushed off with a soft paint brush. A sample of Cotswold limestone, for instance, similar to stone in a building which had been cleaned, though not without difficulty, by the use of caustic soda, was completely cleaned in this way after spraying for no more than half-an-hour. Weathered Caen stone was easily cleaned, without the least damage to the tool marks, after spraying for one hour. A dirty sample of Portland stone required spraying for two hours before all the dirt could be removed with ease, but the stone could have been cleaned at an earlier stage by using stiffer brushes.

Laboratory experiments have also been carried out to imitate the effect of the sulphur pollution of the atmosphere on building stones. In the first series of tests, samples were placed in a vessel and the air was removed from the pores by means of a vacuum-pump. Sulphur dioxide was then admitted until atmospheric pressure was restored, and finally water was allowed to enter the vessel until the stones were covered. After standing for 5 hours the specimens were removed and dried in an oven. This cycle of operations was repeated a number of times.

On sandstones the effect of this treatment was to produce a type of flaking similar to that which occurs in buildings. Skin-formation, very similar to that observed at the original surface of the weathered sandstone, was produced after 13 cycles. After 18 cycles the skin flaked off and exposed the soft powdery surface underneath.

Similar experiments on samples of slate have indicated that it is possible to reproduce lamination in a slate of poor quality.

COLOURINGS FOR STUCCO.—At the present time there is an increasing demand for coloured stuccos and renderings. For the colouring of buff, yellow, green and red stuccos there exists a range of mineral pigments which are fast, both to light and lime, and can be used successfully. The production of a blue stucco has always been difficult. Ultramarine is not stable in contact with lime, although it can be used successfully in renderings, etc., exposed to the air. For use under water (as in swimming baths), where a blue rendering is often desired, it is not suitable. The use of crushed blue glass provides one method for obtaining a blue stucco, but does not fulfil all the requirements.

A method of colouring stuccos, which is of quite a novel character, has recently been tested at the Station. It consists in the use of sand, treated with a metallic oxide to produce a coloured skin, which is stated to be an integral part of the sand grains. The resistance of the coloured sand to alkalis and acids is such that it should be unaffected by the lime and alkalis in cement or by polluted town atmospheres, and there was no indication that the mechanical properties of cement with which it is used would be adversely affected.

Other subjects discussed in the Report are the structure and strength of materials, and the prevention of noise in buildings.

REPORT OF THE FOOD INVESTIGATION BOARD FOR THE YEAR 1936*

THE Report for 1936 contains the general summary of work and an account of the researches in progress by the Chairman, Sir Frank Smith. This is followed by the Report of the Director of Food Investigation (Mr. E. Barnard), in which is recorded the latest progress in those investigations which have not yet reached the stage at which full publication is feasible.

EXPEDITION TO THE DOMINIONS.—Steps are being taken to secure data on the performance of modern methods of gas-storage (*i.e.* in an atmosphere containing about 10 per cent. of carbon dioxide), and in co-operation with the Councils for Scientific and Industrial Research of Australia and New Zealand, an expedition is leaving for New Zealand and Australia in January, 1937. A large programme of work has been planned, embracing the study of conditions in spaces carrying frozen meat, chilled beef in gas-storage, cheese and fruit. The equipment to be carried by the expedition is considerable, and includes some 250 distant-reading electrical thermometers of special construction.

GAS-STORAGE OF PEARS.—The results of the investigations carried out at the Ditton Laboratory during the past few years with the Conference and William's Bon Chretien varieties indicate that the pear responds even more favourably than the apple to gas-storage. These two varieties, at least, can be gas-stored most successfully for several months. After removal from gas-storage the fruit ripens more slowly, and therefore allows more time for marketing, than fruit that has not been stored in this way.

STORAGE OF PLUMS.—The problem of successfully storing Victoria plums for a short period is also one of considerable importance to the grower and distributor. A comprehensive series of experiments, started in the past season, has shown that, at 32° to 34° F., a life of three to four weeks may be expected. Higher temperatures accelerate an abnormal softening of the fruit, and are only suitable for storage for a few days. Close attention must be paid to the degree of ripeness at picking if good quality is to be attained during ripening after storage. If the fruit is picked too green and hard, the flesh becomes soft and jellied at an early stage, especially at 40° F., and although a temperature of 32° to 34° F. holds the change in check to some extent, really good quality cannot be attained. Fruit that was sufficiently mature when picked ripens well after cold-storage at any temperature from 50° F. upwards; if the fruit was immature when picked, a great improvement in colour, and some improvement in quality, can be secured by ripening it at 70° F.

STORAGE OF GRAPES.—A special method that allows water to be supplied to the bunches during storage has been successfully applied in Belgium to the commercial cold-storage of hot-house grapes. Trials of this technique in the laboratory have given promising results with English Muscat grapes, and it is hoped that they may soon be extended on the commercial scale.

RELATIONSHIP BETWEEN PRODUCTION AND STORAGE RESEARCH.—The Board comments on the relationship between the problems of production and those of transport and storage and other post-production processes. Where the agricultural product is to be stored or to receive other special treatment, production and research on production must have that end in view. For instance, the storage of fruit and eggs and the manufacture of bacon from pork clearly introduce new considerations into production that may have an important effect on the course which production takes. Hence, the producers and those responsible for research on production require a specification towards which to work, and the preparation of that specification becomes a task of the Board.

In collaboration with the research institutions represented on the Pig Husbandry Committee of the Ministry of Agriculture and Fisheries, experiments are being carried out on the effect of the breed, growth and feeding of the pig on the quality of the carcase. In addition, investigations on a large scale are being carried out for the Bacon Development Board, on the effect of transport of the pig on the weight of the carcase, and for the Pigs Marketing Board of Northern Ireland, on the differences between the carcases of pigs killed on the farm and in the factory: both Boards are making substantial payments towards the cost of the work. In the course of the year over 800 carcases have been examined.

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* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 3s. 6d. net.

STORAGE OF EGGS AND POULTRY.—Among its other work on the storage of eggs, the quality of eggs stored at 0° C. in atmospheres containing different concentrations of carbon dioxide is being investigated by handling, by tests for palatability, and by the usual chemical and physical tests for the white and yolk. The results so far confirm the view that an atmosphere containing 2·5 per cent. of carbon dioxide improves the quality of the egg, notably in the yolk. Atmospheres containing high concentrations of carbon dioxide, in the range 60 to 100 per cent., affect the quality of eggs uniformly, the yolks being firmer and the whites markedly more liquid than in eggs stored in air. Eggs have been stored in saturated atmospheres within this range for eight months without spoilage by mould or bacteria.

It has been known for some years that eggs retain their fertility longest if they are stored at a temperature of 10° to 12° C. Experiments during the past year have indicated that, at 10° C., the period of fertility can be still further prolonged if the atmosphere contains 2·5 to 5 per cent. of carbon dioxide.

An interesting small trial is recorded in the report on the storage of frozen poultry packed in aluminium foil covered on both sides with waxed paper. Some Sussex cockerels were stored for five months at −10° C. in this way. The birds were thawed, cooked and eaten by several people, who without exception found them excellent in every way, and indistinguishable from freshly-cooked chickens.

STORAGE OF VEGETABLES.—An investigation of the conditions in clamps of potatoes has revealed considerable variation in temperature, sugar-content and sprouting, both between different points in a single clamp and between clamps of different construction. The evidence suggests that improved construction of the clamps may result in better storage of potatoes intended for the manufacture of crisps, and possibly also in improved quality in potatoes held for general domestic use.

Trials of the storage of broccoli have been made with two varieties. A temperature of 32° F. proved best, since higher temperatures reduced the life of the vegetable by accelerating the growth of moulds and yellowing of the leaves. A high humidity is necessary to prevent excessive wilting of the leaves, which would be detrimental to the appearance of broccoli in marketing. At 32° F., and with air of approximately 96 per cent. relative humidity freely circulating in the store, the broccoli kept for three weeks, with three to four days subsequently available for marketing before deterioration set in.

STORAGE OF FISH.—The Report states that herring cured with much less salt than is now employed keep well for six months at −3° C.—a temperature usual in the storage of salt-cured herring. They are very palatable, if a fatty fish is used, but do not develop the full flavour to which the trade is at present accustomed. A certain degree of preliminary ripening at ordinary temperature before the fish is put into cold-storage has been found to improve the flavour, and to bring it nearer to the normal.

Experimental evidence indicates that the rancidity that develops in herring's fat during cold-storage is due to certain enzymes. These are activated by common salt, and this explains the rapidity with which herrings that have been initially frozen in cold brine develop a rancid flavour during storage, particularly if left unglazed. Delay prior to storage has been found to be detrimental; under such conditions a stale flavour, rather than one of rancidity, develops after a few months' storage. It was found, however, that if quite fresh herring were brine-frozen and subsequently well washed, they showed only a slight indication of oxidation of the fat after six months' storage in boxes at −28° C.

Smoke-cured fish (*e.g.* kippers, finnans, fillets of white fish) are usually kept for some months in cold-store at temperatures ranging from −8° to −14° C., with a view to export. Tests at −20° and −28° C. have shown that the quality of the fish is improved by lowering the temperature. This improvement is the result of retarding deterioration, *e.g.* superficial drying, rancidity, development of cold-storage odour and flavour, loss of smoky odour and flavour and colloidal breakdown of the flesh.

Honey Producers' Association

POLLEN ANALYSIS

A MEETING of an informal character, held on May 5th, took the form of a discussion between the members present as to the value of pollen analysis, and in particular of the methods employed by Miss A. Betts and the Rev. Yates Allen, who make analyses for the Association.

Mr. Lindley, the Secretary of the Association, pointed out that admixture of foreign honey with English honey (the mixture being offered for sale as "English Honey") was of common occurrence during periods, such as 1936, when the crops of English honey were small; hence the desirability of the development of a means of detecting such admixture. The method of examination employed by the Association involved the separation of the pollen grains and the examination of their microscopical features in comparison with those of pollens of known origin, the standards consisting either of photomicrographs or of permanent mounts. It was suggested that the adoption of "pollen analysis" by Public Analysts would check the contravention of the Labelling Regulations. The following outline of the method was given:

METHOD OF EXAMINATION.—The honey is diluted with twice its volume of cold or tepid water, and the solution is placed in a tube drawn out at the bottom (such as a milk-sediment tube), and allowed to stand overnight. The pollen grains are removed from the bottom of the tube by means of a pipette and dropped on to microscope slides. The preparation is dried and mounted in either Canada balsam or liquid separated from crystallised honey.

Some doubt was expressed with regard to the efficiency of the sedimentation, as it was pointed out that some workers skim the pollen grains from the top surface of the solution; separation by centrifugal means was regarded as inferior to the sedimentation method.

Miss Betts suggested that the grains should be stained on the microscope stage with concentrated sulphuric acid. The colours acquired by the pollen were an aid to the recognition of the class of plant, if not of the actual plant.

The Rev. Yates Allen said that pollen analysis would enable deductions to be drawn; thus, for example, the recognition of characteristic grains would enable the time of year of the collection of the honey to be decided, and the presence of pollen derived from plants not in flower at that time of year would suggest admixture; this, of course, was only of value for unblended honey.

The general conclusion arrived at was that pollen analysis was of a rather indefinite character, but would be of value if grains characteristic of flowers not found in the stated country of origin were found; for example, grains characteristic of eucalyptus or ti-tree would suggest the presence of Australian or New Zealand honey respectively. Examination of pollen would be of no value in examining a honey labelled "Empire," as the possible sources of origin would embrace an extremely large field.

The examination would require considerable time and skill, as the number of standard pollens was great, and differences of opinion on the origin or presence of a particular pollen would, and did, occur.

Federated Malay States

ANNUAL REPORT OF THE INSTITUTE OF MEDICAL RESEARCH FOR THE YEAR 1936

THE Chemical Division of the Institute for Medical Research (until recently under the direction of the late Mr. R. W. Blair) does work for the Medical and Health services, and deals with exhibits from the Police and samples from other Government departments.

The total number of samples examined was 6564, of which 28 were samples of food submitted under the Sale of Food and Drugs Enactment, 1932.

SIGNATURES ON DOCUMENTS.—Of the 749 exhibits sent by the Police, a large number consisted of documents relating to 21 cases of suspected forgery, anonymous letter-writing, etc. The signatures on several land receipts were photographed under glass plates ruled in small squares. This immediately revealed the unnatural degree of coincidence among the various signatures.

ALGAL CONTROL OF WATER.—The cupri-chloramine treatment, *viz.* the addition of copper sulphate, ammonia and chlorine, has been tried at Gopeng and at the Impounding Reservoir, Kuala Lumpur, the final products being conveyed to ***open*** service reservoirs before passing into supply. In each instance the treatment caused a marked decrease in the algal growth.

TOXICOLOGICAL EXAMINATIONS.—Exhibits relating to 68 cases of poisoning were examined. No poisons were detected in 33 cases. The poisons found included sodium hydroxide in 11 cases, arsenic in 9, and mercuric chloride and morphine in 5 each. Unusual poisons detected were evipan, saponin and margosa oil (1 case each).

NATURE OF THE POWDER IN SHOOTING CASES.—A large number of cartridge cases for shot-guns, rifles and revolvers are now loaded with the so-called "smokeless" ammunition. When this type of cartridge is fired from a gun, it is impossible to say by an examination of the products of combustion found in the barrel how recently the gun was fired. It is frequently stated that the products of combustion of black powder are alkaline and that the products of combustion of smokeless powder are neutral or acid, but it must be remembered that a number of ammunition manufacturers now mix an alkaline substance with their smokeless powders; therefore the mere fact of finding alkaline products of decomposition is no longer an indication of the use of black powder.

CAROTENE-CONTENT OF MALAYAN PALM OIL.—An investigation to determine the variation, if any, in the carotene-content of samples of palm oil, obtained from fruit at different stages of maturity, was carried out by Dr. I. A. Simpson for the Department of Agriculture. The results show that oil of low acidity from fully ripened fruit appears to be richest in this pigment. Attempts to isolate carotene from palm oil have been made, and a satisfactory method has been devised (see *Bull. Institute for Medical Research*, F.M.S., No. 1, 1936).

Western Australia

ANNUAL REPORT OF THE CHEMICAL BRANCH, MINES DEPARTMENT, FOR THE YEAR 1936

THE Chemical Branch of the Mines Department is in control of the Government Laboratory for all the Government departments of Western Australia. The Laboratory is under the direction of Dr. E. S. Simpson.

HORTVET STANDARD.—The bovine milk supply is checked by the staff of the Co-operative Health Board's Laboratory and the Metropolitan Milk Board. In consequence, it is usually only referee or other special samples that are submitted to the Government Laboratory, which possesses the only Hortvet cryoscope in the State. The normal freezing-point for milk has been fixed by a regulation under the Health Act at −0·55° C.

EXCESS OF ALKALI IN TRIPE.—Proceedings were taken by the Department of Public Health for excess alkali in a number of samples of tripe (*p*H greater than 8·0). It was contended in one case by the defence that the moist tripe sample could have derived its alkalinity from the grease-proof paper in which it was wrapped by the inspector prior to being delivered to the analyst. The magistrate declined to record a conviction, although an officer of this branch showed in evidence that grease-proof paper similar to, and from the same supply as that which had been used, was slightly acid, which is the normal condition of most, if not all, of the grease-proof papers on the market.

WHEAT FLOUR IN JAM.—An unusual case of adulteration met with was the addition of starch, in the form of wheat flour, to jam. This was found in the jam of five different varieties made by one firm, evidently having been added for the purpose of thickening.

SULPHITE IN SAUSAGES.—In a case that was referred to the Government Laboratory the question was raised whether sausages containing 9 or 10 grains of sulphur dioxide (as sulphite) per lb. could lose this by decomposition during a period of 40 days in cold-storage. Since the authorities in the literature are divided on this point, experiments were made to determine it. Samples of sausages and sausage meat containing known amounts of a commercial sodium sulphite preservative and of potassium metabisulphite were wrapped in grease-proof paper and then in brown paper bags, sealed and stored for 40 days at about 30° F. The following results (grains per lb.) were obtained:

Preservative added	SO_2 added	SO_2 found immediately	SO_2 after 40 days' storage
Expt. 1—Sausages. Pot. metabisulphite . .	9·0	7·38	6·15
» » . .	3·5	3·23	1·68
Expt. 2—Sausage meat » . .	9·0	7·83	7·06
Expt. 3—Sausages. Sodium sulphite . .	10·5	9·54	10·42
» » » . .	4·0	3·47	3·35

It was concluded that sausages and sausage meat stored for 40 days under the conditions described, retain the greater part of their original sulphur dioxide-content.

QUACK REMEDIES FOR CANCER.—Seven samples of quack remedies, consisting of powders and tablets given by an unauthorised practitioner to a person suffering from cancer, were examined for the Department of Public Health. They consisted mainly of powdered buchu leaves, some with and some without jalap or cascara sagrada. Judging by previous samples from the same source, the prescriber uses these materials as a sort of universal remedy.

"GINGIN DISEASE" OF SHEEP.—An investigation was made to ascertain the cause of "gingin disease" (enzootic ataxia) of sheep. As certain of the pathological symptoms pointed to the possibility of lead being the toxic agent, some work was done on the spectrographic determination of lead, but it was early recognised that the colorimetric dithizone method was more satisfactory. It was shown by this method that specimens from affected lambs and sheep did not contain appreciable quantities of lead in excess of the controls. Livers showed nil to 0·8 parts of lead per million (control *nil*), ribs 4 to 8 (control 2) brain nil to 0·6 (control *nil*). Certain evidence from spectroscopic examination of viscera and the ammonium chloride used in feeding experiments points to a deficiency of copper, and future work will be directed towards elucidating this point.

Spectrographic work to confirm the incidence of cobalt as the responsible factor in the Denmark wasting disease is at present being undertaken.

FRUIT OF THE "QUININE TREE."—A preliminary examination has been made of the fruit of the so-called quinine tree (*Petalostigma quadriloculare*), which is found in Kimberley, north of Wyndham. The fruits, which are orange-yellow when ripe and about one inch in diameter, are extremely bitter, and are said to be a useful medicine and vermifuge for horses. No quinine or other alkaloid was found in the fruits, the bitter taste being due to the presence of a glucoside or other bitter principle.

Physico-Chemical Symbols

REPORT OF A JOINT COMMITTEE OF THE CHEMICAL SOCIETY, THE FARADAY SOCIETY AND THE PHYSICAL SOCIETY

THE Chemical Society, having decided to revise the List of Physico-Chemical Symbols recommended for use in its Journal, invited the co-operation of the Physical Society and the Faraday Society in setting up a Joint Committee to correlate the views of physicists and chemists on symbols for "thermodynamical quantities" and to eliminate as far as possible the confusion which had arisen through the considerable diversity of usage in regard to such symbols.

The Councils of the three societies agreed to this proposal, and in March, 1936, a Joint Committee was set up consisting of: Mr. J. H. Awbery, Prof. F. G. Donnan, Prof. A. C. G. Egerton, Prof. A. Ferguson, Prof. G. I. Finch, Dr. C. F. Goodeve, Prof. C. N. Hinshelwood, Prof. J. R. Partington, Dr. H. J. T. Ellingham (*Hon. Secretary*) and Prof. E. K. Rideal (*Chairman*).

In June, 1936, the Joint Committee presented an Interim Report on the use of symbols for thermodynamical quantities, which, after slight amendment, was approved by the Councils of the three societies.

The Joint Committee was then invited to extend its work to symbols for other quantities of interest to both chemists and physicists, with a view to eliminating conflicts of usage and securing the greatest measure of agreement on the use of physico-chemical symbols.

The present Report to the Councils of the three societies embodies the agreed conclusions of the Joint Committee, including those already given in the Interim Report of June, 1936.

In forwarding this Report to the Councils of the Chemical Society, the Faraday Society and the Physical Society, the Joint Committee recommends:

(1) That the Report be referred also to the Royal Society and the British Standards Institution, so that the comments of these two bodies, together with those of the three co-operating societies, may be available before the Report is finally approved.

(2) That the Report as finally approved be utilised by the three co-operating societies as the basis of any lists of symbols and conventions which they may desire to issue as recommendations for practice in their publications.

In order to consolidate the present step towards uniformity among the three societies, and to facilitate future progress in this direction, it is suggested that:

(a) recommendations of the Joint Committee which are incorporated in the recommendations of one of the individual societies should be specially marked to indicate that they have been approved by both physicists and chemists;

(b) any other recommendations put forward by one of the individual societies should be such as will not conflict with any of the recommendations of the Joint Committee.

(3) That the Report as finally approved be printed (without this preamble), and copies sent for information to the principal societies and organisations in this country and abroad which are likely to be interested. This should help towards securing a greater measure of uniformity among a wider range of scientific and technical bodies in the future.

PART I

The objects of the Joint Committee have been:

(i) To correlate the views of chemists and physicists with regard to the use of symbols for quantities employed in thermodynamics, and to eliminate as far as possible the confusion that has arisen through the considerable diversity of usage in this field (discussed in Part II).

(ii) To deal similarly with symbols for other quantities which are of interest to both chemists and physicists (discussed in Part III).

The Joint Committee has examined the recommendations contained in the published reports of other bodies which have been concerned with symbols in recent years. In regard to symbols for thermodynamical quantities, particular attention was given to the Report on Symbols, Units and Nomenclature of the International Conference on Physics (1934); and in regard to symbols for physico-chemical quantities, to the old "List of Physico-Chemical Symbols" which the Chemical Society has decided to revise, and to a provisional draft of Standard Chemical Symbols and Abbreviations, drawn up recently by the British Standards Institution (largely on the basis of the old Chemical Society list), but held up pending the issue of the present Report.

Through the good offices of Mr. A. Sanford Moss, of the American Standards Association, the Interim Report of the Joint Committee was communicated informally to an "Informal International Conference on Letter Symbols for Heat and Thermodynamics," held in New York in September, 1936; and the Joint Committee has had access to an advance copy of a preliminary Report of this Conference. Consideration has also been given to a "Preliminary List of Abbreviations" recently circulated by the Royal Society.

The Joint Committee has given due consideration to usages adopted by authors of well-known text-books on relevant subjects; and to special lists of symbols in current use by workers in various fields, drawn up by individual members of the Committee.

In submitting this Report the Joint Committee wishes to draw attention to the fact that, although recommendations regarding the use of physico-chemical symbols have been put forward in the past by a number of Committees, these bodies have nearly always been representative of *either* physicists *or* chemists, and not as in the present instance of both.

In carrying out its work the Joint Committee has been guided by the following principles:

(a) Symbols and conventions regarding their use should be chosen from among those already widely adopted, unless there are definite objections to all current usages.

In choosing between possible alternative symbols and conventions preference should be given, in general, to the practice and needs of chemists and physicists, and to practice in English-speaking countries.

It is fully recognised that it would be highly advantageous to secure complete agreement with workers in fields other than chemistry and physics—especially with engineers in regard to thermodynamical symbols. It has to be realised, however, that this involves special difficulties, due not only to the strong feelings which workers in particular fields hold in favour of their accustomed symbols, but also to the limited number of alphabets and founts available for the representation of the large number of quantities to be referred to in the various branches of science and technology. Nevertheless, care has been taken to avoid as far as possible any direct conflict with established usage in related fields, and thus to leave open the way to a wider range of agreement in the future.

Where general agreement on preference for a particular symbol or convention is not reached, alternatives should be given; but one of such alternatives may be indicated as the first preference.

(*b*) Symbols for quantities constituting a well-defined class should, if possible, belong to the same alphabet, fount and case, which should be such as to permit of modification in accordance with a uniform scheme for the representation of any important series of corresponding derived quantities.

Methods of modifying symbols by means of subscripts, superscripts, etc., should be systematised as far as possible.

(*c*) There should be no departure from the standard practice of mathematicians regarding the use of signs, operator symbols, etc.

It is recognised that the detailed recommendations contained in Parts II and III of the Report will not cover all the requirements of workers in any particular field, but it is hoped that they will afford a common basis for practice in a wide range of specialised branches of science.

An important advance towards uniformity of usage will have been achieved if the quantities which appear in the lists below are represented whenever possible by the symbol recommended, or, when this is not possible, by an alternative symbol chosen in accordance with the principles set forth above. It is realised that owing to the limited number of available alphabets many of the symbols appearing in the following lists will have to be used in certain branches of science for quantities which are not referred to in this Report. There can be no objection to this provided that there is no danger of confusion with the quantities which the symbol represents in the lists (given in Parts II and III).

Part II deals with symbols for quantities employed in general thermodynamics, with conventions relating to their use. The lists of symbols recommended are also included in Part III.

Part III relates to symbols for physico-chemical quantities, with conventions relating to their use.

It opens with general recommendations regarding alphabets and founts.

It is recommended that certain important physical constants (*e.g.* Avogadro's number, $\boldsymbol{N}$; velocity of light in vacuo, $\boldsymbol{c}$; electronic charge, $\boldsymbol{e}$; Planck's constant, $\boldsymbol{h}$, gas constant per mol., $\boldsymbol{R}$) should be printed in black italic type.

TO BE PRINTED IN ORDINARY ITALIC, WHEN NOT GREEK

General Physics and Chemistry

Length	l
mean free path of molecules	
height	h
diameter, distance	d
diameter of molecules	σ (sigma)
radius	r
Mass	m
molecular weight	M
atomic weight	A
gram-equivalent weight	Z, J
Time	t
time interval, especially half- or mean-life	τ (tau)
Velocity	v; c ($\boldsymbol{u}$, $\boldsymbol{v}$, $\boldsymbol{w}$)
of ions	u_+ and u_-
angular	ω (omega)
Acceleration	f......$\boldsymbol{a}$
due to gravity (as variable)	g
Force	F, (X, Y, Z)
Moment of inertia	I
Pressure	p, P
especially osmotic	Π (pi)
Volume	v, V
Density	ρ (rho)......d
Compressibility	κ (kappa)......K
Viscosity	η (eta)
Fluidity	ϕ (phi)
Surface area	A......s
Angle of contact	θ (theta)
Surface tension	γ (gamma)...... σ (sigma)
Parachor	$[P]$
Surface concentration excess	Γ (gamma)

Number of mols	n
Concentration, mol fraction	N, x
in other terms	c, C
Solubility	s
Diffusion coefficient	D
Chemical equilibrium constant (products/reactants)	K
solubility product	K_s......L
Velocity constant of chemical reaction	k
Number of molecular collisions per second	Z
Critical energy of activation	E_c
Partition function	f
Efficiency, of any process	η (eta)
Atomic number	Z
Wave function	ψ (psi)

Heat and Thermodynamics

Temperature, on absolute scale (°K)	T
on other scales	θ (theta)......t
Thermal conductivity	k
Energy (general symbol)	E
Work done by or on a system	w......W
Heat entering a system	q
Specific heat	c_p and c_v
molecular heat	C_p and C_v
Latent heat, per g.	l
per mol	L
Intrinsic energy	U......E
Enthalpy, total heat, or heat-content	H
Entropy	S
Free energy (Helmholtz)	A......F
Thermodynamic potential, Gibbs function, free energy (G. N. Lewis)	G
Vapour pressure constant	i
Chemical potential	μ (mu)
Activity	a
coefficient (in terms of molar concentration)	f
Osmotic coefficient	g

Electrochemistry and Electricity

Van't Hoff's factor	i
Degree of electrolytic dissociation	α (alpha)
Valency, or number of charges on an ion	z
Ionic strength	I
Quantity of electricity	Q
especially electrostatic charge	e
Potential (difference)	V
Volta potential	
electrokinetic potential	ζ (zeta)
especially electromotive force of voltaic cells	E
Potential gradient, in electric field	X
Electronic exit work function	ϕ (phi)
Current	I
Resistance	R
specific resistance	ρ (rho)......r
specific conductance	κ (kappa)...... σ (sigma)
Inductance, self	L
mutual	M
Electrostatic capacity	C
Dielectric constant	ϵ (epsilon)
Dipole moment	μ (mu)

Equivalent conductance	Λ (lambda)
equivalent ionic conductance, mobility	l_+ and l_-
Transport number	T_+ and T_-...... n_+ and n_-
Single electrode potential	e (with subscript) ......E (with subscript)
Electrolytic polarisation, overvoltage	η (eta)......π (pi)

Magnetism

Magnetic field strength	H
flux	ϕ (phi)
permeability	μ (mu)
susceptibility, volume	κ (kappa)
mass	χ (chi)
moment	M
induction	B

Optics

Wave-length	λ (lambda)
Frequency	ν (nu)
Intensity of light	I
Refractive index	n......μ (mu) (with subscript)
specific refraction	r (with subscript)
molecular refraction	R (with subscript)
Molar extinction coefficient	ϵ (epsilon)
Angle of (optical) rotation	α (alpha)
specific rotation	$[\alpha]$ (alpha)
Specific magnetic rotation	ω (omega)

To be Printed in Roman, when not Greek

(*a*) *Mathematical Constants or Operators*

Base of natural logarithms	e
Ratio of circumference to diameter	π (pi)
Differential	d
partial	∂
Increment	Δ (delta)
very small increment	δ (delta)
Summation	Σ (sigma)
Function of	f, ϕ (phi)

(*b*) *Examples of Single-Letter Abbreviations* (*cf.* provisional List of Abbreviations drawn up by the Royal Society)

*Ampère (in sub-units)	a.
Volt	V.
Ohm	Ω. (omega)
Watt	W.
Farad	F.
Henry	H.
Centigrade	C.
Fahrenheit	F.
Kelvin	K.
Ångstrom unit	A.
micron	μ. (mu)
metre	m.
gram	g.
litre	l.
Röntgen unit	r.
†Normal (concentration)	N.
†Molar (concentration)	M.

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* *e.g.* "ma." for "milliampère"; but "amp." is preferred for "ampère."

† Separated by a hyphen (and no full stop) from a chemical formula which follows it.

SUBSCRIPTS AND OTHER MODIFYING SIGNS

(*a*) *Subscripts to Symbols for Quantities*

I, II …… 1, 2 ……	*especially with symbols for thermodynamic functions*, referring to different systems or different states of a system.
A, B, ……	referring to molecular species A, B, etc.
i	,, a typical ionic species i.
+, −	referring to a positive or negative ion, or to a positive or negative electrode.
u	referring to an undissociated molecule.
p, v, T	indicating constant pressure, volume, and temperature respectively.
q	indicating adiabatic conditions.
w	indicating that no work is performed.
G, V, L, X	referring to gas, vapour, liquid, and crystalline states respectively.
f, e, s, t, d	referring to fusion, evaporation (vaporisation of liquid), sublimation, transition, and dissolution or dilution respectively.
c	referring to the critical state or indicating a critical value.
o	referring to a standard state, or indicating limiting value at infinite dilution.
p, c, a	*with symbol for an equilibrium constant*, indicating that it is expressed in terms of pressure, concentration, or activity.
C, D, F	*with symbols for optical properties*, referring to a particular wave-length.

Where a subscript has to be added to a symbol which already carries a subscript, the symbol with the first subscript may be enclosed in parentheses with the second subscript outside.

(*b*) *Other Modifying Signs*

o	*as right-hand superscript to symbol*, referring to a standard state.
[ ]	*enclosing formula of chemical substance*, indicating its molar concentration.

Numerals attached to a symbol for a chemical element in various positions have the following meanings:

upper left	mass number of atom.
lower left	nuclear charge of atom.
lower right	number of atoms in molecule.

e.g. $^{7}_{3}\mathrm{Li}$; $^{2}_{1}\mathrm{H}_2$ ($= \mathrm{D}_2$).

British Standards Institution

HAEMACYTOMETER COUNTING CHAMBERS AND HAEMACYTOMETER DILUTION PIPETTES

THE British Standards Institution has just issued a Standard Specification (No. 748—1937) for Haemacytometer Counting Chambers and Haemacytometer Dilution Pipettes, which has been prepared with the co-operation of the medical profession. In framing the specification particular attention has been paid to the various tolerances specified. The accuracy of a blood count depends on the skill of the operator in obtaining a representative sample, in carrying out the dilution, and in the use of the counting chamber. It is also limited by the errors of the apparatus employed. In the preparation of this specification particular attention has been paid to the latter sources of error. The accuracy of the final count depends, for example, on the accuracy of a number of elements of the counting chamber, *e.g.* accuracy of ruling, accuracy of depth, departure of under-surface of cover glass from a plane, etc. In view of the number of possible sources of error, the tolerances on individual elements had of necessity to be kept small in order to avoid the possibility of a comparatively large error in the final count, due to an accumulation of small errors. The Committee, however, did not approach the question of tolerances in a purely theoretical manner. On the basis of measurements carried out at the National Physical Laboratory on samples submitted by manufacturers as representative of current production, the tolerances were also related to the degree of accuracy attainable in manufacture without unduly increasing the cost of production.

Copies of this specification may be obtained from the British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d., post free.

DENSITY-COMPOSITION TABLES FOR SULPHURIC ACID

WHEN the "British Standard Specification for Density Hydrometers" (No. 718—1936) was published, the British Standards Institution announced that density-composition tables for various solutions of industrial importance were in course of preparation. The first of these "British Standard Density-Composition Tables for Aqueous Solutions of Sulphuric Acid for use in conjunction with British Standard Density Hydrometers" (No. 753—1937) has just been published. The tables are based on the International Critical Tables and are very comprehensive. They give percentage compositions (grams of H_2SO_4 in 100 grams of solution) and concentrations (grams of H_2SO_4 in 1 litre of solution) for densities progressing in steps of 0·001 g./ml. from 1·000 g./ml. to 1·846 g./ml. at temperatures progressing by steps of 2° C. from 10° C. to 40° C.

The tables are preceded by explanatory notes. Appendixes to the tables give details of the British Standard density hydrometers available for use in aqueous solutions of sulphuric acid, notes on the reading of British Standard density hydrometers in these solutions, examples of the use of the tables in conjunction with British Standard density hydrometers and details of corrections to hydrometer.

Hydrometer corrections are only necessary when the highest accuracy attainable with the hydrometer is desired. They may often be entirely ignored without prejudice to the degree of accuracy required. For example, over the temperature range 10° C. to 30° C. and for all strengths of acid, the error introduced by neglecting all corrections will not exceed ± 0·001 g./ml. when a British Standard density hydrometer subdivided in 0·0005 g./ml. intervals is used. When this degree of accuracy is adequate, the hydrometer reading may be taken as giving directly the density of the acid in g./ml. at the prevailing temperature of the solution, and the tables give directly the strength of the acid from the ascertained density. No temperature adjustment is necessary and no calculation is required. The use of British Standard density hydrometers in conjunction with the tables provides a concrete example of the simplicity of hydrometry based on density measurements.

Copies of this British Standard Specification (No. 753—1937) may be obtained from the British Standards Institution, Publications Department, 28, Victoria Street, London, S.W.1, price 2s. 2d., post free.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Decomposition Products in Butter and Cream. J. O. Clarke, J. H. Cannon, E. W. Coulter, M. S. Goodman, W. S. Greene, K. L. Milstead, R. L. Vandaveer and J. D. Wildman. (*J. Assoc. Off. Agr. Chem.*, **1937**, **20**, 475–505.)—The indole-content of butter-fat serves as a useful index of the state of decomposition of the cream from which it was prepared. Other useful indications are the acidity of the fat determined by titration of a solution of the fat in benzene with standard sodium ethylate solution and the mould-content determined by the method of Wildman (Abst., ANALYST, 1937, 62, 402). For the determination of indole, the following reagents are required:—Phosphoric-aldehyde mixture made by dissolving 0·4 g. of purified *p*-dimethylaminobenzaldehyde in 5 ml. of acetic acid and mixing the solution with 92 ml. of phosphoric acid (85 per cent.) and 3 ml. of conc. hydrochloric acid; acetic acid and ether mixture made by mixing equal volumes of purified acetic acid and peroxide-free ether; 95 per cent. alcohol (limits 94 to 98 per cent.); dilute hydrochloric acid, by diluting 5 ml. of the conc. acid to 100 ml. with water; standard indole solution made by diluting 100-fold, with 95 per cent. alcohol, a stock solution (stable for 10 days) containing 20 mg. in 200 ml. of 95 per cent. alcohol. In the distillation apparatus all stoppers should be of synthetic rubber. Place 100 ml. of melted butter-fat at about 40° C. in a stoppered measuring cylinder and fill to 250 ml. with 95 per cent. alcohol. Shake the cylinder for two minutes, placing it in water at 60° C. if the fat solidifies, and, when the layers have partly separated, shake for a further two minutes and then allow complete separation to occur. It is important that the fat should remain liquid during the separation. Since indole distributes itself between the two liquids in amounts proportional to their respective volumes, 125 ml. of the alcoholic layer will contain one-half of the indole present. Distil this quantity in steam, collecting 450 ml. of distillate in 90 minutes and maintaining the volume of the distilling liquid at about 70 ml. by the application of heat. Acidify the distillate in a separator with 5 ml. of dilute hydrochloric acid, and extract with 25 ml. of chloroform which has previously been used to rinse out the condenser and receiver. Repeat the extraction with 20 and 15 ml. of chloroform, wash the first two extracts (combined) with 400 ml. of water and extract the wash-water with the third extract. Filter the extract through cotton-wool into a dry 125-ml. separator. To the chloroform extract add 10 ml. of the phosphoric-aldehyde reagent, shake vigorously for two minutes with a frequency of 200 per minute, allow the separator to stand for exactly ten minutes, and separate the acid layer as completely as possible into a glass-stoppered 50-ml. cylinder. Allow the separator to stand for successive periods of two minutes until no more acid liquid can be drained away. The separated acid layer must not contain chloroform, and no attempt to drain acid from the bore of the tap should be made. Dilute the liquid in the cylinder with the mixture of acetic acid and ether first to about 40 ml. and, when cold, to 50 ml. Filter if necessary, using a covered funnel and, within 15 minutes, read the colour of the solution in a photometer fitted with a filter transmitting a narrow band around $500m\mu$. Deduct the result of a blank determination made upon 125 ml. of alcohol in the same apparatus and convert the photometer reading to γ of indole by means of a standard curve constructed by treating the requisite volumes of standard indole solution, diluted to 125 ml. with alcohol, in the same manner as in the blank determination. A series of standards of 1, 2, 5, 7, 10, 15, 20 and 30γ of indole should be made, the blank being deducted from each one. Readings should be taken in cells of about 25, 50 and 100 mm. in length, a separate standard curve being constructed for each cell. The foregoing method is applicable in the presence of various artificial butter flavours and the butter colours used commercially in U.S.A. A more rapid method giving rather higher results may be used in absence of the butter colours Yellow AB and Yellow OB. The butter-fat is treated with alcohol as previously described, and 125 ml. of the alcoholic layer are mixed in a separator with 325 ml. of water, 5 ml. of dilute hydrochloric acid and 25 ml. of chloroform. The procedure is then as before. By another method, also inapplicable to butter coloured with Yellow AB or Yellow OB, and in which strict adherence to detail is necessary, 50 ml. of butter-fat are washed into a separator with 50 ml. of chloroform, 15 ml. of the phosphoric-aldehyde reagent are added, and the mixture is shaken vigorously as in the distillation method. Separation and drainage of the acid layer are carried out as previously described, and the liquid is diluted with the acetic acid and ether mixture first to about 80 ml. and finally to 100 ml. In this method the standard curve is constructed by means of volumes of the standard solution corresponding with 0 to 50γ of indole diluted to 100 ml. with chloroform.

It was found that lactic acid fermentation of cream with pure cultures caused no increase in the indole-content and acidity of the butter made therefrom. Decomposition induced by inoculation of sterile cream with decomposing cream caused increased acidity of the fat, increased mould-content and sometimes increased indole-content. When commercial cream was exposed to an environment favourable to decomposition, the acidity, mould-content and indole-content increased both in the cream and the butter, the rate of increase being more rapid with higher temperature. No significant changes in these indications were noted in butter stored under conditions imitating commercial shipping or storage. The indole-content of commercial butter of good quality is of the order 4 to 6γ per 50 ml. of fat. A. O. J.

Hydrolysis of Potato Starch by Malt Amylase at Different Temperatures. J. L. Baker and H. F. E. Hulton. (*J. Inst. Brewing*, 1937, **43**, 301–307.)—Malt amylase was prepared by grinding 100 g. of a pale English malt (diastatic power, 25° Lintner) with 300 ml. of 20 per cent. alcohol, and precipitating the filtered extract with three times its volume of 95 per cent. alcohol, the resulting precipitate being separated in a centrifuge and dissolved with the amylase solution in 100 ml. of water. A 3 per cent. paste of pure potato starch farina was digested (at the rate of 0·5 ml. per g. of starch and at *p*H 6·5) for 1 or 12 hours at 15·5°, 50°, 65° and 74° C. The cleavage products were then evaluated, the sp.gr., dissolved solids (using the factor 3·93), $[\alpha]_D$ and copper-reducing power (Fehling's) being determined; in the last instance the results obtained by Lane and Eynon's volumetric method were expressed as a percentage of anhydrous maltose (*R*) on the solids found by means of the factor 3·93, and they are accurate to within 2 per cent. Fractionation experiments with 90 per cent. alcohol and fermentation tests using a pure culture of *S. cerevisiae* were also made. Maltose and probably one dextrin only (*R*, 10; $[\alpha]_D$, 185–190, approximately) are produced as the sole ultimate products of conversions made at temperatures up to 50° C., the whole of the "apparent maltose" being fermentable; above 50° C., and definitely at 65° and 74° C., maltodextrin is also present in addition to these substances. The evidence for the presence of the maltodextrin is that (*a*) part of the "apparent maltose" is unfermentable (and this corresponds with the maltose portion of the maltodextrin); (*b*) those fractions which are soluble in alcohol, or have been freed from maltose by fermentation, indicate the presence of a complex which is not maltose but which is soluble in alcohol and unfermentable, and the constants of which have the mean values *R* 35 and $[\alpha]_D$ 174, *i.e.* intermediate between those of maltose and dextrin. The extent of the formation and survival of this maltodextrin is dependent on the temperature of conversion, being negligible at 15·5° and 50° C., definite at 65° C., and very marked at 74° C. (when only 50 per cent. of the "apparent maltose" is free, *i.e.* fermentable, maltose). The well-known inhibiting effect of high temperatures on the saccharifying activity of malt amylase provides a probable explanation why maltodextrin is found only in starch conversions which have been carried out at such temperatures. Thus, although the maltodextrin is probably an intermediate compound which is formed in starch conversions at all temperatures, it is converted into maltose by amylolytic hydrolysis at 15·5° and 50° C.; at higher temperatures this cannot occur, and the maltodextrin, therefore, accumulates in the final products. J. G.

Seeds and Oil of *Rhus glabra*. G. H. McFadden and R. L. McMurray. (*Amer. J. Pharm.*, 1937, **109**, 397–406.)—The fruits of *Rhus glabra*, or Sumac berries, were collected in Ohio, shelled and air-dried, and the cleaned fruits were powdered. They contained 5·25 per cent. of moisture, and gave on extraction with ether a total extract of 17·27 per cent. They contained 31·86 per cent. of crude fibre, 21·61 per cent. of pentosans, 1·32 per cent. of total nitrogen; arsenic, none; total ash, 2·55 per cent. Petroleum spirit extracted from the cleaned ground fruits 12·42 per cent. of oil with the following characteristics:—sp.gr. at 20° C., 0·9227; n_D^{20}, 1·4719; $[\alpha]_D^{20}$, 0·00; saponification value, 168·17; iodine value, 87·17; ester value, 159·2; acid value, 8·9; unsaponifiable matter, 2·67 per cent. The percentage composition of the ash was: sand, 2·95; silica, 7·44; iron, 0·86; Al_2O_3, 4·67; CaO, 22·80; MgO, 7·24; Mn_3O_4, 0·147; copper, nil; zinc, 0·078; Na_2O, 4·16; K_2O, 38·15; Cl, 1·58; SO_3, 7·15; P_2O_5, 21·17. The pure oil obtained by steam-distillation of the crude oil, solution in petroleum spirit and washing with water, amounted to 94·6 per cent. of the crude product, and was blackish-brown with a green fluorescence; saponification value, 176·7; iodine value, 94·15. The aqueous fraction contained tannin and sugar. The sterol acetate obtained from the unsaponifiable matter had m.p. 117° to 118° C., and a hydrocarbon (hentriacontane), m.p. 68° C., was obtained from the alcoholic filtrate from the digitonin treatment. The solid and liquid fatty acids were separated, and the liquid acids identified were linolic and oleic acids. The methyl esters of the solid fatty acids were repeatedly fractionally distilled until 8 well-defined fractions were obtained. The acids identified were *n*-butyric (small quantity), palmitic, lignoceric and (probably) arachidic acids. D. G. H.

Fatty Oil from the Seeds of *Valerianella olitorea*, Poll. A. Steger and J. van Loon. (*J. Soc. Chem. Ind.*, 1937, **56**, 298–300T.)—The fruits of *Valerianella olitorea*, the corn salad, were crushed and extracted with ether, yielding 14 per cent. of oil. The kernels alone gave 38·7 per cent. of a nearly colourless oil, and the shells contained some 4 per cent. of a dark green oil. By running through a mill, sieving and winnowing, kernels with a very small quantity of shell may be isolated, yielding 23–24 per cent. of a light-coloured oil (B). Oil (A) was from hand-selected kernels and oil (C) from the hulls.

	Oil A	Oil B	Oil C
Sp.gr. at 78/4° C.	0·8830	0·8800	0·9200
n_D^{70}	1·4575	1·4582	1·4620
Saponification value	192·6	190·5	205·4
Iodine value (Wijs)	145·2	144·9	116·5
Thiocyanogen value	84·2	84·2	67·7
Acid value	1·2	3·7	48·1

Thin films of oils A and B dried in 2 days on glass plates at 45° C. in diffused daylight; oil C did not dry. The compositions of oils B and C (the fatty acids being calculated from the iodine and thiocyanogen values and proportion of saturated acids) were:—unsaponifiable matter, 1·2, 2·6; glyceryl (as C_3H_5), 4·2, 3·5; volatile and insoluble products, 1·8, 19·8; saturated acids, 11·5, 15·2; oleic acid, 18·0, 7·6;

linolic acid, 52·7, 47·9; linolenic acid, 10·6, 2·4 per cent. The extraction residues of the two oils contained, respectively, moisture, 10·0, 9·7; ash, 7·1, 6·8; nitrogen, 3·0, 1·15; protein, 18·8, 7·2; crude fibre, 25·9, 34·2; nitrogen-free extract, 38·2 and 42·1 per cent. The cake from oil B was found to be suitable for cattle feeding, that from oil C for manure. D. G. H.

Oil from the Seeds of *Blepharis edulis*. G. P. Pendse and J. B. Lal. (*J. Indian Chem. Soc.*, 1937, **14**, 362–366.)—A bitter glucoside (blepharin) and *dl*-allantoin have already been isolated from the seeds of *Blepharis edulis* (*J. Indian Chem. Soc.*, 1936, **13**, 109), and the composition of the oil has now been investigated. Extraction of the powdered seeds with benzene yielded 3·8 per cent. of a thick reddish-brown oil with the characteristic odour of the drug. The purified oil had the following characteristics:—sp.gr. at 28° C. 0·9332; $[\alpha]_D^{28}$, − 8·4; n_D^{30}, 1·4846; viscosity (*cf.* with rape oil), 8·35; solidifying pt., − 3° C.; saponification value, 186·5; iodine value, 90·8; Hehner value, 91·65; acetyl value, 11·54; acid value, 11·85; unsaponifiable matter (including phytosterol), 2·5 to 3·0 per cent. The fatty acids were separated by Twitchell's method into 12·38 per cent. of saturated (iodine value 2·6; mean molec. equiv. 276) and unsaturated acids, 87·62 (iodine value 104·7; mean molec. equiv. 270·2). The unsaturated acids consisted of 83·45 per cent. of oleic and 16·37 per cent. of linolic acid. The saturated acids were converted into the methyl esters, and 4 fractions were separated by fractional distillation. Palmitic, stearic and arachidic acids were identified. A light brown solid deposited from the oil was for the most part soluble in boiling alcohol, yielding a crystalline phytosterol which appeared to be identical with arnidiol described by Klobt (*Compt. rend.*, 1904, **138**, 763; **140**, 1700). D. G. H.

Oil from the Seeds of *Solanum nigrum*. G. P. Pendse. (*J. Indian Chem. Soc.*, 1937, **14**, 367–370.)—*Solanum nigrum* (Gurkamai and Choti Makoi in Hindustani) is cultivated in India for its medicinal properties, and is described by Dymock in *Pharmacographia Indica*, 1891, **2**, 549, and by Basu and Kirtikar, in *Indian Medicinal Plants*, 1918, **2**, 889. The active principle of the fruits is solanine. The fresh fruits yielded 30 per cent. of juice, 3·75 per cent. of dried husk and 9·5 per cent. of seeds. The powdered seeds on extraction with petroleum spirit gave about 2 per cent. of a greenish-yellow oil with the characteristic odour of the drug. The purified oil had the following characteristics:—sp.gr. at 30° C., 0·8964; $[\alpha]_D^{28}$— 6·61; n_D^{30}, 1·4436; viscosity (compared with rape oil), 7·12; solidifying pt., − 7° C.; saponification value, 184·7; iodine value, 111·7; Hehner value, 93·10; acetyl value, 9·97; acid value, 2·4; unsaponifiable matter, 1·4 to 1·6 per cent. The fatty acids consisted of 5·88 per cent. of saturated (iodine value 3·6; mean molec. equiv. 180·4) and 94·12 per cent. of unsaturated acids (iodine value 114·8; mean molec. equiv. 176·6). The unsaturated fatty acids consisted of 73 per cent. of oleic and 27 per cent. of linolic acid. No linolenic acid was found. The saturated acids were converted into the methyl esters which were fractionally distilled; only palmitic and stearic acids were found. The unsaponifiable matter deposited from ether in silky flakes, m.p. 127° to 129° C., and the acetyl derivative of the sterol had m.p. 119° to 120° C., with $[\alpha]_D^{32}$, in alcoholic solution − 30·5°. D. G. H.

Colorimetric Determination of Morphine. D. C. Garratt. (*Pharm. J.*, 1937, **139**, 193.)—The accuracy of the B.P. colorimetric determination of morphine can be increased by "compensating" the blank solution, after it is made ammoniacal, with a quantity of the test solution equal to that used in the test. The necessity for this "compensation" is shown by the brown colour given by the extracted alkaloidal residue with ammonia without addition of nitrite. Except for aromatic powder of chalk and opium, for which it requires further modification, the method may be used for all galenicals, including mixtures of opium and ipecacuanha, for the latter does not interfere with the test. In aromatic powder of chalk and opium the phenolic constituents of the aromatics give a colour similar to that obtained with morphine, but these may be eliminated by extraction with ether *after* the lime solution has been made ammoniacal with ammonium sulphate; the morphine remains in the aqueous phase, and is extracted as usual with chloroform in the presence of alcohol. S. G. S.

Relationship between the Constitution of Tragacanth Gum and the Viscosity of its Mucilage. J. M. Rowson. (*Quart. J. Pharm.*, 1937, **10**, 161–176.)—The object of this work was to compare the bassorin and methoxyl contents and saponification values of a number of gums with the viscosities of the mucilages prepared from them. It is the insoluble bassorin in tragacanth which absorbs water and gives the mucilage its viscosity, the influence of the small quantity of soluble gum present in a pharmacopoeial mucilage being only slight. The direct determination of bassorin by physical methods (*e.g.* separation by filtration or centrifuging, and subsequent weighing) was unsuccessful, and Ogle's method (*Pharm. J.*, 1889, **20**, 3) was therefore modified so as to overcome the difficulty of the variable hydrolysis of the bassorin and the consequent production of soluble decomposition products; the amount of bassorin was found by subtracting the percentages of moisture and soluble gum (tragacanthin) from 100. A 0·1 per cent. mucilage was prepared by shaking a weighed quantity of gum with a little alcohol in a dry graduated flask, adding distilled water, and shaking well. After it had stood for 48 hours, with occasional shaking, it was filtered by suction through a double layer of filter-paper into a dry suction flask; 100 ml. of clear filtrate were then evaporated on the water-bath in a tared flask, and the residue was dried in a water-oven and weighed to obtain the tragacanthin-content. Variable results obtained in duplicate determinations on the same gums could not be traced to impurities in the solvents, or to variations in the areas or capacities of the funnel and vessels used, but appeared to occur when the time elapsing between the preparation of the mucilage and filtration exceeded 48 hours. Further experiments showed that it is therefore desirable to boil the mucilage for exactly 3 minutes, in order to attain the maximum particle size and degree of hydration and, therefore, the maximum viscosity and minimum soluble extract; if this period is exceeded, the bassorin is hydrolysed and forms soluble products, which increase the apparent tragacanthin-content. The use of freshly-boiled and cooled distilled water is also recommended. The moisture was determined at 100° C., and also in a vacuum desiccator over sulphuric acid; the latter procedure gave higher results and is preferable. The average tragacanthin and bassorin contents of 12 powdered gums ranged from 9·52 and 75·47 to 12·62 and 75·57 per cent., respectively, but no direct mathematical ratio could be traced between the bassorin (when expressed as relative percentages of an arbitrary standard) and the corresponding viscosities (6·26 to 1064·0 poises for a 1·25 per cent. mucilage). There is evidence, however, for the generalisation that the mucilage from a gum with a low bassorin-content will have a low viscosity or suspending-power, and that, although the determination of the bassorin-content is of value for distinguishing between a good and a poor gum, the viscosity depends on the properties as well as on the quantity of the bassorin present. The B.P. (Zeisel) method for the determination of the methoxyl-content was used, 1 g. of the sample and 50 ml. of a 0·1 *N* solution of silver nitrate being taken; the excess of silver nitrate was titrated with a standard solution of ammonium thiocyanate in the presence of strong nitric acid. Replicate tests made in this way agreed well, and the average values found ranged from 0·763 to 4·426 per cent. (4·70 to 7·03, if expressed as a percentage of the bassorin-content). A close proportionality exists between the bassorin and methoxyl contents of the gums examined; the latter value is therefore a satisfactory measure of the former, and the conclusions as to the relationship of the methoxyl-content to the viscosity are the same as for the bassorin-content. The changes produced in a gum by the action of heat appear to be (*a*) partial demethylation of bassorin, which forms products which are insoluble in water, but do not swell readily in it, and therefore, yield mucilages of low viscosity; (*b*) complete demethylation of bassorin, the resulting products being soluble in water, but incapable of exerting much effect on the viscosity of a mucilage compared with that due to the methylated compounds. The saponification value was determined on 1 g. of sample, which was heated for 1 hour under a reflux condenser with 100 ml. of water and 25 ml. of 0·5 *N* potassium hydroxide solution; the cooled solution was titrated back with acid, 5 ml. of a solution of phenolphthalein being necessary on account of the colour of the liquid. The average results for 5 gums ranged from 222·0 to 256·5; they showed no relationship either to the bassorin or methoxyl contents or to the viscosities. It is suggested that the B.P. monograph on tragacanth should be modified to require a bassorin-content of not less than 60 per cent. when determined by the process described above, and a methoxyl-content (Zeisel method) of 3·75 per cent., and that a concentration of not more than 1·65 per cent. of gum should be required to produce a mucilage having a viscosity of 400 poises when measured by means of 5/32 in. steel spheres falling in a sphere viscometer at 20° C. The mucilage for this purpose should be prepared in a bulk of 600 ml. by the dry-flask process, and should be allowed to stand for 48 hours before the measurement is made. A description of the falling-sphere viscometer and the method of calculating viscosities by the Ladenburg formula should be inserted in an appendix to the Pharmacopoeia (*cf.* Brindle and Rowson, *Quart. J. Pharm.*, 1936, **9**, 161). J. G. [illegible]

Estimation of Acriflavine and Related Compounds in Pharmaceutical Preparations and Surgical Dressings. G. F. Hall and A. D. Powell. (*Pharm. J.*, 1937, **139**, 195–196.)—The solution obtained by a preliminary treatment of the dressing or galenical, and containing between 0·02 and 0·2 g. of the diaminoacridine derivative, is diluted to approximately 200 ml., and adjusted until the reaction is faintly acid to Congo red paper. One g. of sodium acetate crystals is added, followed by sufficient excess of $M/50$ potassium ferricyanide solution (19 ml. to 30 ml. according to the amount required for precipitation) with stirring during the addition. The mixture is allowed to stand for 30 minutes and is then filtered through a Buchner funnel. The precipitate is washed with three successive quantities of 10 ml. of water, and to the combined filtrate and washings are added 5 ml. of conc. hydrochloric acid, 1 g. of sodium chloride, 0·5 g. of potassium iodide and 5 ml. of a 30 per cent. solution of zinc sulphate, the contents of the beaker being well mixed after each addition. After 3 minutes the liberated iodine is titrated with $N/100$ sodium thiosulphate solution. A blank determination is also made. Each ml. of $M/100$ ferricyanide solution precipitated is equivalent to 0·00888 g. of acriflavine, 0·00779 g. of euflavine or 0·00921 g. of proflavine. For the assay of medicated gauze, 20 g. or other convenient quantity are extracted in a Soxhlet extractor with 95 per cent. alcohol slightly acidified with hydrochloric acid (250 ml. of alcohol and 2 ml. of 10 per cent. hydrochloric acid). After about 3 hours the extract is transferred to a beaker, 50 ml. of water are added, and the bulk of the alcohol is evaporated. To the hot liquid 25 ml. of chloroform are added and the whole is mixed thoroughly. After cooling, the mixture is transferred to a separator and allowed to separate, and the removal of the fats is completed by a further two extractions with 25 ml. of chloroform. The combined chloroform extracts are washed twice with 10 ml. of water which has been acidified with one or two drops of dilute hydrochloric acid. The united aqueous solution is evaporated to a small volume to remove the alcohol, then diluted to about 200 ml., made slightly acid to Congo red paper, and treated as described above.

Fatty and oily preparations are prepared for the assay by dissolving 25 g. to 50 g. in about 50 ml. of chloroform. This solution is extracted with 20 ml. of water containing 2 ml. of 10 per cent. hydrochloric acid, followed by two extractions with 10 ml. of water containing 0·5 ml. of the dilute hydrochloric acid. The combined aqueous extracts are washed with 25 ml. of chloroform; any medicament taken into the chloroform is extracted with 10 ml. of water containing one or two drops of hydrochloric acid solution. The combined aqueous extracts are evaporated sufficiently to remove alcohol if present, cooled, diluted to about 200 ml., treated with dilute sodium hydroxide solution until the reaction is only slightly acid to Congo red paper, and examined by the general method. Glycogelatin preparations present certain difficulties, but the following treatment was found satisfactory with glycogelatin pessaries. About 15 g. to 30 g. of the sample are dissolved in 100 ml. of warm water, and the gelatin is precipitated by the addition of 200 ml. of 95 per cent. alcohol. The mixture is cooled, the precipitate is coagulated by stirring, removed by centrifuging, re-dissolved in 50 ml. of water and re-precipitated with 100 ml. of alcohol. The clear alcoholic liquids are combined, evaporated to remove the alcohol, and diluted to 200 ml. with water. After the acidity has been adjusted the general method is followed. S. G. S.

Biochemical

Conversion of Stearic Acid into Palmitic Acid in the Organism. R. Schoenheimer and D. Rittenberg. (*J. Biol. Chem.*, **1937, 120,** 155–165.)—Palmitic acid was isolated from the carcases of mice which had been fed for 5 days with deuterostearic acid. The deuterium-content of the palmitic acid indicated that it had been derived from the stearic acid. The separation was obtained by fractional distillation of the methyl esters. This was done in a distillation apparatus which is described, and which is capable of separating the higher fatty acids from a mixture of 1 to 3 g. A method is also described for the removal of a contaminating deutero substance from another one. S. G. S.

Amino Acid Catabolism. The Fate of Certain Synthetic α-Amino Acids Administered by Subcutaneous Injection to the Normal Dog. J. A. Leighty and R. C. Corley. (*J. Biol. Chem.*, 1937, **120**, 331–334.)—When amino acids were injected into a normal dog under the experimental conditions described it was found that those acids having a straight carbon chain readily lost their nitrogen, which was excreted as urea. The presence of a methyl group on the same carbon acid as the nitrogen retarded the loss of nitrogen, while the presence of the methyl group on the carbon atom adjacent to the one with the amino group prevented deamination. This latter effect was probably due to spatial configuration. S. G. S.

Determination of Thiocyanate in Tissues. B. B. Brodie and M. M. Friedman. (*J. Biol. Chem.*, 1937, **120**, 511–516.)—Thiocyanate in tissues may be determined by placing 0·5 g. to 1·0 g. of finely hashed and thoroughly mixed wet tissue, or 100 mg. to 300 mg. of the dried pulverised tissue, in a 125-ml. Erlenmeyer flask and adding 20 ml. of alcoholic potash solution (40 g. KOH in 1 litre of 95 per cent. ethyl alcohol). The flask is attached to an air condenser, and the mixture is digested on a steam-bath for 30 minutes. The flask is then emptied into a 200-ml. evaporating dish, and rinsed out into the dish with alcohol, then with water, and finally again with alcohol. The dish is placed on the steam-bath and the alcohol is evaporated. The residue is washed with small amounts of water into a 25-ml. graduated cylinder. One drop of phenolphthalein solution is added, the volume is diluted to 20 ml., and the whole is transferred to a 125-ml. Erlenmeyer flask. The cylinder is washed with exactly 3 ml. of water, and this is added to the solution in the flask. The liquid is neutralised with 4 *N* nitric acid, the amount required being noted, and 0·5 ml. is added in excess. To this acid solution 1 ml. of 10 per cent. sodium tungstate solution is added dropwise, the flask being shaken during the addition. Sufficient water is added to give a total volume of 30 ml., but since the measurement of the total volume is difficult on account of frothing, the amount of the water required is ascertained by the careful measurement of the wash-water, the nitric acid and the sodium tungstate solutions. The flask is then stoppered, shaken vigorously, and left for 10 minutes. The mixture is filtered, and a 25-ml. portion of the filtrate is transferred to a 100-ml. beaker; a turbid filtrate is not objectionable. The solution is neutralised with a 10 per cent. aqueous solution of caustic potash, and 0·5 ml. is added in excess. The pigments in solution are removed by adding 1 g. of Norit carbon and heating to boiling, with constant stirring. The mixture is filtered hot into a 100-ml. beaker, and the carbon is washed four times with 5-ml. portions of water. If the filtrate is still coloured, this treatment must be repeated. The colourless filtrate is evaporated to about 5 ml. and cooled, and to it is added 0·5 ml. of 4 *N* nitric acid. The solution is then quantitatively transferred to a 25-ml. glass-stoppered graduated flask, diluted to 20 ml., and the ferric thiocyanate colour is developed by the addition of 4 ml. of the ferric reagent. After thorough mixing, the resulting solution is compared with a standard in a colorimeter. Should a turbidity occur on acidification with the nitric acid, the ferric thiocyanate solution is filtered into the colorimeter cup. The standard is prepared by putting an amount of standard solution containing approximately the same amount of thiocyanate as occurs in the unknown into a graduated cylinder, adding 1·5 g. of potassium nitrate, 0·5 ml. of 4 *N* nitric acid, water to make up 20 ml., and then 4 ml. of the ferric reagent. If the volume of the standard differs from that of the unknown, the ferric reagent is added in the ratio of one volume of reagent to 5 volumes of solution, and the amount of potassium nitrate added is such that its concentration is equal to that in the unknown.

The ferric reagent is prepared by dissolving 100 g. of ferric nitrate, $Fe(NO_3)_3.9H_2O$, in 1 litre of water, adding 50 ml. of conc. nitric acid with shaking, and diluting to 2 litres. For the standard thiocyanate solution, 14 g. of sodium thiocyanate are dissolved in 1 litre of water. This solution is standardised against silver nitrate solution and is kept in a brown bottle in an ice-box. The solution changes slowly and occasional standardisations are necessary. Weaker solutions, which do not keep, are prepared from this. The sensitivity of the test is such that 75γ of thiocyanate per g. of wet tissue may be determined. The average error ranged from 8 per cent. on 75γ to 2 per cent. on 350γ. The thiocyanate-content of rat tissue varied from 0·56 mg. per g. of dry tissue for muscle to 4·26 mg. per g. for blood. S. G. S.

Use of Mercuric Salts and Nitrous Acid in the Colorimetric Determination of Tyrosine and Tryptophane present in Solution. J. W. H. Lugg. (*Biochem. J.*, 1937, **31**, 1422–1433.)—The Folin and Ciocalteu method for estimating tyrosine, which is based on the Millon reaction, was found to be unsatisfactory when applied to the hydrolysates of plant leaf proteins, as the unknown colour solutions were cloudy. The difficulty has been overcome by changes of procedure, embracing mercuration of the tyrosine and precipitation in one step of any tryptophane present, and dilution of the reacting mixture with a solution approximating closely to it in composition. The liquids under investigation are separated from suspended solids by centrifuging for 10 minutes at 1500 times gravity being usually sufficient. A glass rod of 2-mm. diameter, slightly bent at the end, is used to stir the solutions and to suspend precipitates in them. Barely moistened with octyl alcohol it serves as a whisk to force solids at the air-liquid interface beneath the surface before centrifuging. It is rinsed down with a few drops of the appropriate solution. The aliquot portion of test solution (up to about 3 ml.), together with sufficient 5 *N* sulphuric acid solution to bring it to *p*H 0·3 (found by the titration of a separate aliquot portion with the use of an indicator, such as brilliant cresyl blue), is diluted to 5 ml. with *N* sulphuric acid solution in a 15-ml. centrifuge tube. Five ml. of a mercury solution (75 g. $HgSO_4$, 55 g. $HgCl_2$, 70 g. Na_2SO_4 in 850 ml. of water; addition of 128 g. of 98 per cent. H_2SO_4 and dilution to 1 litre) are added, and the tube is maintained at 60° to 65° C. in a water-bath for 30 minutes. It is then cooled in a water-bath for 1 hour at 1° or 2° C. below room temperature, and, after centrifuging, the clear liquid is drained into a 25-ml. graduated cylinder. The precipitate in the centrifuge tube is treated with 10 ml. of a solution prepared by diluting the mercury solution with an equal volume of *N* sulphuric acid. Any precipitate is well stirred, and the tube is again centrifuged. The liquid is drained as before into the cylinder, the contents of which are diluted with the wash solution to 24·5 ml. in readiness for the tyrosine estimation. A standard is prepared simultaneously with the unknown solution in an entirely analogous manner. The precipitate remaining in the tube is used for the tryptophane estimation.

For the estimation of the tyrosine the contents of the graduated cylinders should be employed within an hour, as cloudiness may develop on long standing. Into each cylinder 0·5 ml. of a solution of sodium nitrite (*M*/1) is run slowly so as to float on top, and as soon as possible the cylinders are shaken simultaneously. Colorimetric comparison of the unknown with the standard should be made 3 minutes after the mixing. For the estimation of the tryptophane the mercury precipitate, which may be left moist in the tube for a day without detectable destruction, is well rubbed up with 10 ml. of a solution prepared by dissolving 12 g. of mercuric sulphate and 9 g. of mercuric chloride in 600 ml. of water plus 100 g. of 98 per cent. sulphuric acid and then adding a further 500 g. of sulphuric acid, with cooling, and diluting the mixture to 1 litre. The centrifuge tube is kept at 40° to 45° C. in a water-bath for 15 minutes, with occasional rubbing of any solid that separates. It is then cooled in a water-bath for 30 minutes at 1° or 2° C. below room temperature and, after centrifuging, the clear liquid is drained into a 25-ml. graduated cylinder. A further 10 ml. of the mercury solution is run into the tube, the contents are stirred, any separating solid is well rubbed for a few minutes, and, after centrifuging, the liquid is drained into the cylinder, and the volume is made up to 24·5 ml. with the same solution. Within about an hour 0·5 ml. of the sodium nitrite solution is run into each cylinder so as to float on the top, and as soon as possible both tubes are shaken simultaneously, and the colorimetric comparison is made with the least delay. The standard tyrosine solution contains 0·25 to 1·0 mg. per ml. in either 0·1 *N* sulphuric acid or 0·05 *N* caustic soda solution; it keeps for several months. The standard tryptophane solution is of the same strength, with water as the solvent; it deteriorates to the extent of about 1 per cent. at 20° C. in a week. The errors are less than 1 per cent. for tyrosine and less than 2 per cent. for tryptophane, and the recovery of added tyrosine and tryptophane was within these limits. S. G. S.

Bacteriological

Use of Brilliant Green—Eosin Agar and Sodium Tetrathionate Broth for the Isolation of Organisms of the Typhoid Group. E. R. Jones. (*J. Path. and Bact.*, 1936, **42**, 455–467.)—The brilliant green—eosin agar is made by the addition of 1 per cent. of lactose, 0·09 per cent. of eosin and about 0·006 per cent. of brilliant green to proteose agar with *p*H 7·4. As the combined inhibiting effect of eosin and brilliant green varies with different batches of these dyes, the optimum quantity of brilliant green for the suppression of *B. coli* and the growth of *B. typhosus* is determined experimentally as follows:—Five tubes of melted agar, each containing 20 ml., are set up in duplicate in a rack and maintained at 55° C. One ml. of a 20 per cent. solution of lactose and 0·6 ml. of a 3 per cent. aqueous solution of eosin are added to each, and finally 0·2, 0·4, 0·6, 0·8 and 1·0 ml. of a 0·1 per cent. aqueous solution of brilliant green severally to each of the five tubes. The plates are poured and allowed to set, and a weak suspension of *B. coli* is spread over one half and a similar suspension of *B. typhosus* over the other. That dilution is chosen which gives the best suppression of *B. coli* and growth of *B. typhosus*. When the number of typhoid bacilli is likely to be small, the use of this medium may be combined with a tetrathionate broth enrichment medium made as follows:—To 90 ml. of ordinary broth are added 2·5 g. of chalk previously autoclaved, 10 ml. of a 60 per cent. solution of sodium thiosulphate (sterilised by steaming for 30 minutes), and 2 ml. of a 30 per cent. solution of iodine (iodine 6 g., potassium iodide 5 g. and water to make 20 ml.). This medium is distributed in 5-ml. lots. For use, 0·5 g. of faeces is emulsified in 5 ml., from this a 1 : 10 dilution is made in the same broth, the two are incubated overnight at 37° C., and brilliant green—eosin agar plates are spread from each tube. It is claimed that this medium is suitable for the isolation of typhoid, paratyphoid and the Salmonella bacilli, and that it is at least as good as, if not better than, Wilson and Blair's bismuth sulphite—brilliant green—agar and free from the disadvantages of the latter, *viz.* complexity, loss of selective properties on keeping, and longer time required for incubation before colonies become characteristic. D. R. W.

A Satisfactory Method of Isolating Tetanus Organisms from Mixed Material. Eric C. Giller. (*Amer. J. Hyg.*, 1937, 26, 394–400.)—The method of injecting mixed cultures into laboratory animals with a view to demonstrating characteristic spasm-producing toxin is criticised on the ground that other organisms interfere with the production of, or destroy such toxin, and the necessity for the isolation of *Cl. tetani* for the performance of the test with pure cultures is emphasised. For the separation of obligatory anaerobes from facultative anaerobes the method suggested by Hall (1919) of using a dye for the elimination of all aerobes was found to be entirely satisfactory, and for the isolation of tetanus organisms from a mixed culture of anaerobes the method of Fildes (1925), which takes advantage of the tendency of these organisms to grow in a thin film on the surface of peptic blood infusion agar, spreading to the very apex of the slant, was found to be of great value. The procedure finally adopted was briefly as follows.—The material (street dust of the city of Baltimore) suspended in normal saline was heated to

80° to 82° C. for 1 hour, transferred to Bengston's cooked meat medium (previously heated to 100° C. for 15 minutes), layered with vaseline, and incubated for 8 days. A portion was withdrawn, heated to 80° C. for 15 minutes, sown into glucose broth containing crystal violet in concentration 1 : 100,000 (previously heated to 100° C.), layered with vaseline and incubated for 18 hours at 37° C. Transfers were then made to aerobic agar slants, crystal violet dextrose broth and Holman's meat tubes. The aerobic slants show whether the aerobes are eliminated, the crystal violet broth provides for repetition if they are not, and the Holman's meat tubes provide a viable culture if they are. Sub-culturing from the dye-broth tube in the three separate media was repeated if necessary to three, four or five transfers (usually three sufficed) to eliminate aerobes. After elimination of all aerobes, peptic blood infusion agar (Fildes' influenza medium, 1920) slopes were inoculated in their condensation water and incubated for 3 to 4 days in a MacIntosh and Fildes' jar. The tubes were then carefully examined with a lens for film-like growth at the apex of the slopes. In 8 of the 63 samples from which tetanus bacilli were finally isolated they were isolated from the first slopes; in the remainder they were isolated only after re-sowing in the condensation water of another slope several times in succession. Aerobic control tests were also made. From the last series of tubes the uppermost film of growth was transferred to Holman's meat medium layered with vaseline and incubated for 3 days at 37° C. The strains isolated were identified as *Cl. tetani* by their morphology, cultural reactions, and the toxicity test for pathogenic action, which is described in another contribution (see next Abstract). D. R. W.

Study of the Biochemical Reactions of Strains of *Cl. tetani* isolated from Street Dust. E. C. Giles. (*Amer. J. Hyg.*, 1937, **26**, 401–415.)—Twelve strains of proved purity were studied. The characters used in their identification were their morphology, staining reactions, motility, biochemical reactions and pathogenicity. The biochemical tests were directed to the determination of the proteolytic and saccharolytic properties of the strains, the media employed being Hall's modification of Von Hibler's brain medium, Robertson's egg-cube broth and alkaline egg broth, litmus milk, gelatin, and plain broth containing 1 per cent. of one of the following substances—lactose, maltose, dextrose, xylose, mannitol and dulcitol. A detailed description of the action of the strains on these media is given. Variations in the reactions similar to those recorded by other observers occurred, so that hard and fast rules cannot be laid down. The general conclusion arrived at was that *Cl. tetani* has feeble proteolytic properties and does not ferment carbohydrates, the apparent gas production (without acid) observed with three strains being attributed to action on the broth medium. Even pathogenicity showed variation; nine strains produced a spasm-producing toxin neutralised by tetanus antitoxin, but three did not. One of the strains that produced no such toxin also failed to liquefy gelatin and produced acid and gas in glucose and maltose and was therefore regarded as *Cl. pseudo-tetanus*. For the pathogenicity test the strains were grown anaerobically in Holman's meat medium for 10 days at 37° C. and, after standing overnight, 0·3 ml. of the clear supernatant liquid was inoculated intramuscularly into the right thigh of white mice. Control tests were made with white mice which had been given, one hour before receiving the same dose of culture fluid, 0·3 ml. of antitoxin containing 700 units per ml. Paralysis and death within 96 hours was the result recorded after injection with toxic strains without antitoxin.

D. R. W.

Errata

September issue.

p. 671, 3rd line from bottom. In the sentence "toxins produced by members of the food-poisoning or dysentery groups" *omit* "toxins produced by."

October issue.

p. 753, line 3, *for* "50 to 90 bacteria per gram" *read* "50 to 90 millions."
,, ,, 5, *for* "both" *read* "broth."

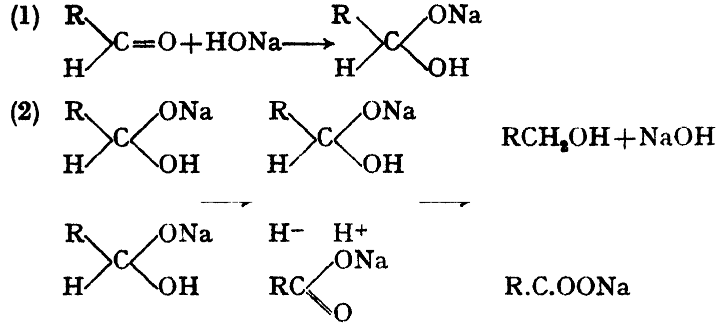
Organic

Dehydration of Ether. N. Schoorl. (*Pharm. Weekblad.*, 1937, **74**, 1108–1109.)—Anhydrous sodium sulphate is not completely satisfactory for the dehydration of ether for extraction purposes. It is more efficient when the water is present in suspension as fine droplets (when it acquires 10 mol. of water of crystallisation) than when the water is present in solution (*cf. id.*, 1910, **47**, 963; and von Siebenrock, *Monatsh. f. Chem.*, 1909, **30**, 759). The use of ignited gypsum ($CaSO_4,\frac{1}{2}H_2O$), which is converted eventually into $CaSO_4,2H_2O$, has also been suggested, but the objection here is the formation of the intermediate hydrate $CaSO_4,1{\cdot}5H_2O$ which resists further absorption of water. Anhydrous magnesium sulphate is preferred, as it will remove about two-thirds of the water present. The inverse relative efficiencies of these three dehydrating agents, expressed in terms of the vapour tensions of the water in the respective hydrated salts, are approximately 0·76 : 0·94 : 0·21. Ether containing over 0·6 or over 0·35 per cent. of dissolved water gives a turbidity when shaken with twice its volume of carbon tetrachloride or carbon disulphide, respectively. These reagents give positive results with ether saturated with water (*i.e.* containing 1 per cent. of water) after it has been treated with sodium sulphate or calcium sulphate, but if magnesium sulphate has been used, no turbidity is produced when the amount of water has been reduced to about 0·35 per cent.

J. G.

Catalysis of Cannizzaro's Reaction by Active Nickel and Platinum. Application to some Aldoses. M. Delépine and A. Horeau. (*Bull. Soc. Chim.*, 1937, **4**, 1524–34.)—Experiments with formaldehyde, butaldehyde, and benzaldehyde showed that these aldehydes, if shaken in solution with sodium hydroxide solution and Raney nickel, give Cannizzaro's reaction, and the corresponding acids and alcohols can be detected in the liquid. Extending the experiments to aldoses, the authors worked with galactose, glucose, and arabinose. In a typical experiment, 18 g. of galactose and 100 ml. of $N/2$ sodium hydroxide solution were shaken with 4·5 g. of nickel. The alkalinity of the liquid decreased rapidly, the volumes of $N/10$ sulphuric acid required to neutralise 1 ml. of the solution after a few seconds, 2 hours, 4 hours, and 6 hours being respectively

4·5 ml., 2·5 ml., 1·8 ml., and 1·25 ml. The solution gave 5 g. of dulcitol and (by treatment with cadmium chloride) 4·2 g. of cadmium galactonate. Glucose gave sorbitol and gluconic acid, and arabinose yielded arabitol and arabonic acid. When Vavon platinum was used as the catalyst, hydrogen was evolved, and the alcohol and acid corresponding to the sugar were formed. In one experiment, 18 g. of galactose, 1·5 g. of platinum, 100 g. of water, and 5 ml. of sodium hydroxide solution were shaken in an atmosphere of hydrogen; after 1 hour a further 5 ml. of alkali solution were added. One litre of hydrogen was evolved, and 14 g. of calcium galactonate and 2·2 g. of dulcitol were isolated from the liquid. If the quantity of platinum is reduced, a smaller volume of hydrogen is evolved and larger quantities of alcohol and acid are formed. The hydrogen formed during the reaction can be used to reduce an easily hydrogenisable substance added to the system, as was shown by shaking 18 g. of galactose, 7 g. of crotonic acid (as the sodium salt), 8 ml. of 10 N sodium hydroxide solution and sufficient water to bring the volume up to 250 ml., with 4·5 g. of nickel. After 8 hours 5 ml. of butyric acid and 14 g. of calcium galactonate were isolated. The following reactions are suggested in explanation of the phenomena.



If the hydrogen ions are not fixed with sufficient rapidity, molecular hydrogen is evolved. E. M. P.

Needle Shellac. E. Stoch. (*Färb.-Ztg.*, 1937, July 31st ; *Chem. Trade J.*, 1937, **101**, 114.)—This product is prepared (*Belgian Pat.*, 413,775, 1936) by spinning the shellac into filaments, which are subsequently broken up into "needles." It contains only 2 per cent. of water, as compared with 25 and 5 per cent. in button- and in powder- or leaf-shellac, respectively, and it therefore keeps well without special precautions. Its large surface area per unit weight also ensures that it dissolves rapidly without agglomeration of the needle-clusters, even when very concentrated solutions are being made. The samples of ruby and bleached needle shellac examined gave a negative reaction for rosin and a positive Tschirch reaction; their analytical values were in close agreement with those obtained for the various grades in their usual commercial forms, the only exception being that the ash-contents of the needle shellacs were slightly higher. Examination of the fluorescence produced in ultra-violet light provides the best method of distinguishing needle shellac from the other grades, and the original paper (in the *Farb.-Ztg.*) gives the results so obtained with solutions in a wide range of organic solvents. J. G.

Polymerisation of Tobacco Seed Oil. M. Brambilla and G. Balbi. (*Chim. e Ind.*, 1937, **19**, 373–377.)—The recorded values for the composition of tobacco seed oil (*Nicotiana tabacum*) are as follows:—palmitic acid, 32 to 40 per cent.; oleic acid, 24·5 to 30 per cent.; linolic acid, 15 to 20 per cent.; unsaponifiable matter, 1 to 1·5 per cent. As in previous work on seed oils by the same authors (ANALYST, 1936, **61**, 716, 855) tobacco seed oil was polymerised at high temperatures (333° to 337° C.) and at lower temperatures (297° to 300° C.). The polymerisation products obtained at the higher temperatures are unsuitable for industrial application. The following table shows the effect of polymerisation at 297° to 300° C. on refined pressed and extracted oils:—

	Sp.gr. at 20° C.	n^{20}_{D}	Viscosity, η_{20}	Acid value	Iodine value	Colour (Hellige colorimeter)
Expressed oil	0·9220	1·4789	58·31	0·47	93·5	0·51
polymerised, 6 hours ..	0·9289	1·4842	1280·3	7·59	89·52	1·93
" 7 hours ..	0·9301	1·4864	2027·8	9·27	79·81	2·13
" 8 hours ..	0·9387	1·4883	3848·1	11·42	72·27	2·41
Extracted oil	0·9298	1·4782	53·29	0·88	94·5	0·68
polymerised, 6 hours ..	0·9349	1·4848	1213·4	7·33	91·14	2·33
" 7 hours ..	0·9370	1·4866	1990·0	9·04	80·74	5·50
" 8 hours ..	0·9403	1·4898	3793·1	11·33	74·31	7·44

The colour values were obtained by comparison with a standard potassium dichromate solution (3·863 g. in 1 litre of water); the figures in the table were calculated by dividing 100 by the thickness, in mm., of the oil layer.

Further experiments, in which acids and colloidal substances were added to the refined oils before polymerisation, showed that the colloidal substances present in crude oils are the cause of their comparatively smaller tendency to polymerise. The general conclusion drawn from the results of the experiments is that the polymerised oils obtained at the lower temperatures are semi-drying stand-oils suitable for use in varnishes; their low acidity is a particularly useful property.

E. M. P.

Colorimetric Determination of Carbon Disulphide in Gas or Motor Fuels. Chem. Dept. South Metropolitan Gas Co. (*J. Soc. Chem. Ind.*, 1937, **56**, 287–290T.)—A modification of the diethylamine test is based on the reaction between piperidine and carbon disulphide. Monochlorobenzene is substituted for alcohol as solvent, and cupric oleate for cupric acetate, since the latter is insoluble in chlorobenzene. The apparatus for measuring the colour consists of three compartments bored out of square oak blocks, the lowest containing a 6-volt 6-watt lamp mounted at the focus of a silver lacquered parabolic reflector to give an approximately parallel beam of light. A diaphragm between this chamber and the next restricts the beam, and on the diaphragm rests a crystallising dish, 7 cm. in diameter, in which a coloured salt may be used as a light-filter. Above this is an iris diaphragm on which the dish (with a flat base with an area of about 20 sq. cm.) containing the test liquid rests. Mounted in the hinged lid of the top compartment is the light-sensitive cell, connected with a 0–100 micro ammeter (resistance 100–150 ohms). Fifty ml. of copper sulphate solution containing 100 g.

of the pentahydrate per litre are placed in the filter-dish, and 25 ml. of heavy medicinal paraffin are floated on the surface to restrict evaporation. The coloured test solution is poured into its dish, and the same volume of a blank solution of the reagents free from carbon disulphide is put into a second dish of the same dimensions. The iris is closed and the lamp is lighted; after 3 minutes the dish and blank solution are placed centrally in the top compartment, and after 15 seconds the iris is adjusted to give a reading of exactly 100 microamperes. The test-dish is substituted for the blank and the reading is again taken after 15 seconds. The instrument is calibrated by a series of tests upon known weights of carbon disulphide from 0 to 1·5 mg. The solutions required are (1) piperidine in chlorobenzene: 20 ml. per litre; (2) cupric oleate in chlorobenzene: 2·5 g. per litre; (3) carbon disulphide in chlorobenzene: 0·2 g. per litre. Ten ml. of solution (1) are mixed with 5 ml. of solution (2) and a measured volume of solution (3) is added. The mixture is diluted to 25 ml. with chlorobenzene and the light transmission is measured. The colour obtained with a given weight of chlorobenzene should be measured within 30 minutes of its formation. A 1 per cent. solution of piperidine in chlorobenzene is satisfactory for the removal of carbon disulphide from gas, even when present in concentrations as low as 0·2 grain per 100 cb. ft., and gas containing an equivalent of 30 grains of sulphur per 100 cb. ft. when passed at a rate of 1 cb. ft. per hour through two piperidine washers in series gave practically no carbon disulphide in the second washer. In period tests the gas should be pre-dried with calcium chloride. Carbonyl sulphide gives a colour similar to that given by carbon disulphide, but it is much less stable; mercaptans do not seriously affect the test; thiophene is without effect, but hydrogen sulphide must be removed by a lead carbonate tower. Details for the determination of carbon disulphide in coal gas are given for a short period (15 minutes) test, and for long periods. For short period tests the mixture of solutions is placed in a dry gas washer of the boiling-tube type, the inlet tube terminating in a bulb with pinholes. The gas is passed through the apparatus at the rate of 1 cb. ft per hour and the amount of that leaving the outlet is recorded by a meter. To determine carbon disulphide in benzole and other hydrocarbon oils, a measured volume of oil is added to the mixed reagent (20 ml. of solution (1) and 5 ml. of solution (2)) and the colour is measured as described. D. G. H.

Colour Reaction of Woody Tissues with Chlorine and Sodium Sulphite. W. G. Campbell, S. A. Bryant and G. Swann. (*Biochem. J.*, 1937, **31**, 1285–1288.)—A qualitative study has been made of the well-known reaction of woody tissues with chlorine and sodium sulphite. The reaction, which is probably specific for phenolic bodies containing the 1 : 2 : 3-trihydroxybenzene nucleus such as tannic acid and pyrogallol, is given by hot and cold aqueous extracts of wood, by the acid filtrate from lignin determinations, and even by cold aqueous extracts of isolated sulphuric acid lignin itself. It is therefore probable that phenolic compounds, which may be either tannins or even a form of lignin, permeate the structure of certain hard woods and soft woods, and that these survive, in part at least, the conditions used in the isolation of lignin by means of conc. sulphuric acid. S. G. S.

Determination of Alkali in Wool. D. E. Stocker. (*J. Soc. Dyers and Col.*, **1937**, **53**, **348–349**.)—A weighed quantity of wool is dried and extracted continuously with absolute alcohol, any free caustic alkali being then determined by titrating the extract with 0·1 *N* hydrochloric acid, with phenolphthalein as indicator. The extract is then evaporated, and a solution of the residue in water is treated with acid, which decomposes any soap. The fatty acids from the soap may then be extracted with ether, the residue from the evaporation of this extract being dissolved in alcohol and the fatty acids determined by titration in the usual way. The extracted wool is soaked for several hours in a 1 per cent. solution of boric acid, and transferred with the solution to a small tap-funnel in which is a plug of glass wool. The stem of the funnel is inserted in the rubber bung of a suction filter-flask, and the liquid is drawn out. The tap of the funnel is closed, water is introduced, and, after thorough stirring, the tap is opened and again the liquid is drawn out. After ten such washings the united filtrates are titrated with 0·1 *N* hydrochloric acid, with methyl red or methyl orange as indicator. If the calcium soaps or dyestuffs are present, the boric acid solution and the wash-water should be saturated with salt, and the difficulty of titrating a coloured liquid does not arise. Other advantages are that boric acid has no action on the indicators used, that adsorption of the acid by the wool does not affect the results, and that sodium borate is easily removed from the wool by the washing process. The method is more easy to manipulate than the terephthalic acid method of Hirst and King (ANALYST, 1926, **51**, 212), and the necessity for a separate determination of calcium soaps, which are also decomposed by terephthalic acid and must therefore be allowed for, is eliminated. When 5·0 ml. of 0·1 *N* sodium carbonate solution were allowed to dry into 1·0 g. of purified wool, the quantities found (4 experiments) ranged from 4·7 to 4·9 ml. When purified wool was treated with 10 ml. of 0·2 *N* borax solution and extracted as described above, the amount recovered was equivalent to 9·9 ml. of 0·2 *N* hydrochloric acid. J. G.

Weighting of Indian Silk. C. R. N. Reddy and B. S. Srikantan. (*J. Indian Chem. Soc.*, 1937, **14**, 371–375.)—The conditions for weighting Indian silk (Eri silk and Mysore-Japanese varieties) have been ascertained. The weighed silks (0·5 g.) were immersed in 50 ml. of the weighting solution (lead acetate), washed, dried at 78° C. in an air-oven for 1 hour and weighed. The optimum *p*H of the bath was found to be 8·0; weighting occurs chiefly in the first half-hour, and prolonged treatment has a detrimental effect on the quality of the silk, rendering the appearance dull. Maximum weighting occurred when the lead acetate solution had sp.gr. 1·25 and a further increase in the concentration had no effect. The best results were obtained at 28·5° C., and higher temperatures affected both the tensile strength and appearance of the silk. Eri silk had a higher weighting capacity than Mysore-Japanese, but it acquired an undesirable deep colour and lost tensile strength. By washing after weighting and immersing for 5 minutes in a fixing bath of sodium hydrogen phosphate, washing again, and repeating the process until the fibres were adversely affected, it was found possible to weight a Mysore-Japanese silk to 105 per cent. D. G. H.

Inorganic

Colorimetric Determination of Copper as Ferrocyanide. H. Hahn, R. Juza and R. Langheim. (*Z. anal. Chem.*, 1937, **110**, 270–275.)—The flocculation of copper ferrocyanide is delayed by gelatin. The neutral copper solution is treated with 2 per cent. acetic acid (5 ml.), 10 per cent. ammonium acetate solution (5 ml.), 1 per cent. gelatin solution (10 ml.), and 0·2 per cent. potassium ferrocyanide solution (10 ml.), and diluted to 50 ml. The tint should be matched within an hour against water and the blue-green filter S50 of the Pulfrich photometer. Unduly large quantities of other electrolytes (alkali and ammonium salts) should not be present. A large excess of lead (1000 parts to 1 of copper) may be present without interfering, lead ferrocyanide being comparatively soluble in presence of excess of ammonium acetate. W. R. S.

Colorimetric Determination of Cadmium as Sulphide. R. Juza and R. Langheim. (*Z. anal. Chem.*, 1937, **110**, 262–270.)—The procedure utilises gelatin as a protective colloid in ammoniacal cyanide solution. The neutral solution is treated with 1 per cent. ammonia solution (1 ml.), 10 per cent. potassium cyanide solution (4 ml.), 10 per cent. ammonium sulphate solution (1 ml.) and 1 per cent. gelatin solution (1 ml.), diluted to 30 ml., and poured into a 50-ml. flask containing 5 ml. of saturated hydrogen sulphide water. The volume is adjusted, and the colour matched after 15 minutes' standing. This is done against water with a Zeiss photometer and the blue filter S43. A considerable amount of zinc in the solution (1000 parts to 1 of cadmium) does not interfere with the determination; the solution is titrated with the cyanide solution until the zinc precipitate re-dissolves. After addition of an excess of 4 ml. of cyanide solution, the determination is conducted as described above. If copper is present (maximum, 10 parts to 1 of cadmium), the ammoniacal solution is decolorised by cyanide, after which 4 ml. of cyanide solution are added. The determination can be made in presence of nickel (maximum, 100 parts) and cobalt (10 parts). An allowance may be necessary for the yellow tint of the nickel or cobalt cyanide solution containing the excess of cyanide prescribed above. W. R. S.

Determination of Platinum and Gold, and Detection of Platinum Metals. S. O. Thompson, F. E. Beamish and M. Scott. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 420–422.)—The crystals formed by heating a slightly acid solution of platinum chloride with dimethylglyoxime on a steam-bath for several hours were found to be of fairly definite composition, corresponding closely with $PtC_8H_{14}N_4O_4$; the precipitation, however, was incomplete. The addition of an excess of dimethylglyoxime in alcoholic solution to a gold chloride solution acidified with hydrochloric acid gave a yellow precipitate. The mixture was boiled for 30 minutes, and the precipitate was filtered off, washed with water and finally ignited, giving metallic gold. The recovery of gold in this way was found to be quantitative. Various tests available for the detection of the platinum metals are described. New tests for osmium are as follows:—(1) An aqueous solution of pyrogallol produces a blue colour with a solution of sodium osmate. "If a drop of hydrochloric acid is added to the test solution followed by a drop of conc.

pyrogallol solution, a definite colour is obtained if the test solution contains 0·01 mg. of osmium per ml." Rhodium and iridium do not interfere, but palladium and platinum give brown colours, and gold gives a purple colour. (2) Ephedrine hydrochloride gives an orange colour with alkaline sodium osmate solution. The sensitiveness of the test is improved by extraction of the coloured compound with carbon tetrachloride; 0·01 mg. of osmium per ml. produces a faint colour. Platinum and rhodium give no colour. Palladium and gold give a very faint yellow colour, but the test is not sensitive for these metals, nor for iridium, which gives a faint green colour under the same conditions. S. G. C.

New Fluorescence Test for Aluminium. C. E. White and C. S. Lowe. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 430–431.)—The orange-red fluorescence produced under ultra-violet light by Pontachrome Blue Black R dye (the zinc salt of 4-sulpho-2,2′-dihydroxy-azonaphthalene) with aluminium is a highly sensitive test and can be used to detect aluminium in the presence of beryllium. The solution to be tested should first be made alkaline with sodium hydroxide, any precipitate formed being filtered off and rejected. Sexavalent chromium must be reduced and fluorides must be removed. The solution is then acidified with acetic acid, and 0·5 ml. of a 0·1 per cent. solution of the dye is added. With solutions of aluminium as dilute as 1 p.p.m., half-an-hour should be allowed for the fluorescence to develop. The fluorescence is preferably observed in a dark room under a quartz mercury vapour lamp equipped with a Wood's glass filter. The maximum sensitiveness of the test under these conditions was found to be 0·2 p.p.m. of aluminium, but with this extreme dilution it was necessary to keep the solution overnight for the fluorescence to develop. Quartz containers for the test solution had no advantage over those of soft glass. With argon bulbs as a source of ultra-violet radiation, the sensitiveness of the test was much less, being 10 p.p.m. of aluminium. Highly coloured ions, such as copper, chromium, iron, nickel and cobalt, masked the fluorescence, but precipitation with sodium hydroxide as described above, removed the interference. Fluoride interferes, but may be removed satisfactorily by precipitation as calcium fluoride. The following ions (amounts not stated) did not interfere in the test: beryllium, gallium, indium, thallium, silver, mercury, lead, bismuth, cadmium, arsenic, antimony, tin, zinc, calcium, strontium, barium, magnesium, sodium, potassium, ammonium, lithium, rare earths, chloride, nitrate, sulphate, phosphate, tartrate. S. G. C.

Determination of Gallium in Germanite. F. Sebba and W. Pugh. (*J. Chem. Soc.*, 1937, 1371–1373.)—Previous analyses of germanite (*e.g.* ANALYST, 1925, **50**, 91) involved decomposition with acids and have given gallium results which the authors consider low. They decompose the finely powdered ore (5 g.) by fusion with sodium hydroxide (10 g.) in an iron crucible. The cooled melt is extracted with water, and the residue is collected, washed with water, and rejected. The filtrate contains the germanium, arsenic, and a little molybdenum as thio-compounds, as well as the whole of the gallium; it is treated with sufficient hydrochloric acid to produce 2 *N* acidity, and boiled for the coagulation of the sulphide precipitate with simultaneous solution of a little adsorbed gallium; there is sufficient sulphide in the fusion extract to remove all the arsenic at this stage. The precipitate is collected, and the filtrate is neutralised to methyl red with sodium hydroxide. The precipitated gallium hydroxide is collected, dissolved in hydrochloric acid, and the solution is evaporated to dryness to eliminate traces of germanium and dehydrate silicic and tungstic acids. The filtered solution still contains a trace of lead and molybdenum which are removed by another treatment with alkali sulphide and acidification, with intervening filtration to eliminate lead sulphide. Filtration of the acidified liquid eliminates molybdenum sulphide. The gallium is precipitated in the filtrate by means of cupferron (*cf.* ANALYST, 1933, **58**, **111**). The procedures described above gave concordant results of 1·2 per cent. Ga.

W. R. S.

Gravimetric Determination of Lithium as Aluminate. H. Grothe and W. Savelsberg. (*Z. anal. Chem.*, 1937, **110**, 81–94.)—The procedures based on precipitation as fluoride, phosphate, and lithium zinc uranyl acetate were re-investigated and found to be unreliable except in certain special cases, and hence not adapted for general work. A new method was worked out in which the lithium is precipitated as aluminate (solubility 0·09 g. per litre), which is ignited and weighed as $2Li_2O{\cdot}5Al_2O_3$. Lithium factor 0·0488. Dobbin and Sanders have proposed the use of the same compound for the determination of aluminium (*J. Amer. Chem. Soc.*, 1932, **54**, 178; Abst., ANALYST, 1932, **57**, 197).

The reagent is prepared from 50 g. of potash alum dissolved in 900 ml. of warm water. The cooled solution is stirred and treated with a strong solution of 20 g. of sodium hydroxide until the precipitate re-dissolves completely. After standing overnight the liquid is filtered and diluted to 1 litre, the *p*H having previously been adjusted to 12·6. This is ascertained electrometrically by measurement of the potential of an antimony electrode against a calomel electrode. A close adjustment of the *p*H concentration is necessary for the complete precipitation of the lithium without co-precipitation of aluminium hydroxide.

The lithium solution is adjusted to *p*H 3 with the aid of colour indicators, treated in the cold with 40 ml. of reagent per 10 mg. of lithium, re-adjusted electrometrically to *p*H = 12·6 by means of *N* sodium hydroxide, and filtered after a short time. The precipitate is washed with cold water, by decantation first, until the washings no longer redden phenolphthalein, ignited, and weighed. The results of six test analyses show errors varying from + 0·52 to − 1·04 per cent., with a mean error of − 0·27 per cent.

W. R. S.

Elimination of Phosphate in Qualitative Analysis. L. W. N. Godward and A. M. Ward. (*J. Chem. Soc.*, 1937, 1337–1338.)—The scheme is based on the precipitation of ammonium phosphomolybdate. The filtrate from the hydrogen-sulphide group is boiled with nitric acid, and a small portion is tested for phosphoric acid by the molybdate reaction. Another portion is treated with ammonia; if no precipitate is formed, or a precipitate soluble in excess, the solution is treated with ammonium sulphide for the zinc group. If a permanent precipitate is formed with ammonia, the bulk of the filtrate is treated with a little sulphuric acid and 1 g. of ammonium sulphate, and any sulphate precipitate is collected and tested for barium and strontium. The filtrate is diluted to 25 ml. and treated with 5 ml. of strong nitric acid and 5 g. of ammonium nitrate. An excess of solid ammonium molybdate (1·7 g. for 0·1 g. P_2O_5) is stirred into the boiling solution, and boiling is continued for 5 minutes. The solution is filtered, and the filtrate is tested for complete precipitation. After cooling, a very slight excess of strong ammonia is added. Any precipitate is collected and tested for iron, aluminium and chromium; the filtrate is tested with ammonium sulphide for the zinc group. It remains to test the filtrate from the zinc group for calcium and magnesium. The liquid is acidified and boiled, and the molybdenum sulphide is filtered off. The filtrate is boiled with sodium perborate and hydroxide until colourless, after which boiling is continued to the destruction of the perborate. The liquid is then acidified with hydrochloric acid, boiled, filtered, made ammoniacal, treated with 5 g. of ammonium acetate and 10 ml. of 6 per cent. ammonium molybdate solution in dilute ammonia, and boiled gently for 10 minutes. The white precipitate is calcium molybdate, which is confirmed by solution in dilute sulphuric acid and precipitation with ammonium oxalate. The filtrate from the calcium molybdate is treated with a solution of *p*-nitrobenzene-azoresorcinol, followed by sodium hydroxide until the colour of the dye changes; a blue gelatinous precipitate indicates magnesium. W. R. S.

Volumetric Determination of Selenium by the Norris and Fay Method. W. C. Coleman and C. R. McCrosky. (*Ind. Eng. Chem., Anal. Ed.*, **1937**, **9**, **431–432**.)—The method originally due to Norris and Fay (*Amer. Chem. J.*, **1896**, **18**, 705; Abst., ANALYST, **1897**, **22**, 82) involves the titration of selenious acid with sodium thiosulphate, the reaction proceeding according to the equation:

$$4Na_2S_2O_3 + H_2SeO_3 + 4HCl \rightarrow Na_2SeS_4O_6 + Na_2S_4O_6 + 4NaCl + 3H_2O.$$

The procedure, as slightly modified by the present authors, is as follows: To the selenious acid solution (150 ml.) containing the equivalent of 5 ml. of 6 *N* hydrochloric acid, some starch indicator solution is added, and the liquid is titrated with standard sodium thiosulphate solution (0·1 *N*) added in 5-ml. portions; a few drops of potassium iodide solution (2·5 per cent.) are added after each 5-ml. addition of thiosulphate solution, and the titration is stopped when the potassium iodide addition no longer produces a local starch-iodide blue. The solution is then over-titrated, an excess of not more than 5 ml. of thiosulphate being present. The excess of thiosulphate is back-titrated with standard iodine solution until a blue colour is produced. The thiosulphate solution may be standardised against elemental selenium as follows:—The selenium (0·35 to 0·45 g.) is dissolved in 5 ml. of 10 per cent. sodium cyanide solution by heating, the solution is diluted to 250 ml., and a 50-ml. aliquot portion is evaporated to 20 ml. Two ml. of a filtered 1 per cent. solution of gum arabic and 5 ml. of 5 *N* hydrobromic acid are added. A precipitate of red selenium is thus produced, and is kept colloidally dispersed by the gum arabic. A rapid stream of air is bubbled through the solution for 15 minutes to remove most of the hydrocyanic acid. Most of the selenium is oxidised by adding, drop by drop, a saturated solution of potassium bromate. When only a little red selenium remains, 0·1 *N* potassium bromate solution is added, the disappearance of the red colour marking the completion of the oxidation to selenious acid. A few drops of a saturated alcoholic solution of acetanilide are added to discharge any excess of bromate, and the liquid is heated to boiling.

After cooling, the solution is diluted to 150 ml., and the selenious acid is titrated as described above. The accuracy of the titration process on the basis of the stoichiometric reaction is within 1 part in 1000. The temperature of the solution titrated may vary from 0° to 20° C., but it is essential that the excess of thiosulphate used be limited in the manner indicated, as a large excess introduces an error, owing to its decomposition in the acid solution. Hydrobromic, sulphuric or perchloric acid may be used instead of hydrochloric acid in the titration liquid; nitric acid, acetic acid and phosphoric acid were found to be unsatisfactory. Small amounts of selenium may be determined by the use of 0·01 N or 0·001 N thiosulphate solution, the only modification being that a 25 per cent. solution of potassium iodide is employed instead of the 2·5 per cent. solution as indicator.

S. G. C.

Microchemical

Systematic Semi-micro Procedure for the Qualitative Analysis of the Commoner Cations. J. H. Winkley, L. K. Yanowski and W. A. Hynes. (*Mikrochem.*, 1936, **21**, 102–116.)—A scheme of analysis is given for the following cations: silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, iron, chromium, aluminium, zinc, manganese, calcium, barium, strontium, magnesium, potassium, sodium, lithium and ammonium. Spot tests are used directly, and not merely as confirmatory tests, but not for the members of the alkaline earth and alkali groups. The solutions used contained sufficient amounts of the nitrates and chlorides to furnish concentrations of 10 mg. of the cations per ml. The maximum initial volume of solution employed in any analysis was never more than 0·2 ml.; the amount of any cation present in the solution never exceeded 2 mg. A complete list of the concentrations of test substances and reagent solutions is given. The reagents are those found to give best results with relatively inexperienced workers.

J. W. M.

Micro-determination of Chloride in Biological Fluids with Solid Silver Iodate. J. Sendroy. (I) Gasometric Analysis. (*J. Biol. Chem.*, **1937**, **120**, 335–403.)—Small amounts of chlorine in biological fluids may be determined by the following general procedure:—The sample is diluted in an acid solution (usually with 0·085 M phosphoric acid) to a *p*H between 2·0 and 3·0 and to a chloride concentration between 0·012 and 0·003 M. Solid silver iodate is then added, with vigorous shaking, which causes the precipitation of the chloride and the release of iodate into the solution. The precipitate of silver chloride and the excess of silver iodate are removed from the solution by centrifuging. The supernatant liquid is then analysed gasometrically for iodate by means of an alkaline hydrazine solution. For details of the method and for the calculation of the results, the original paper should be consulted.

(II) Titrimetric Analysis. (*Ibid.*, 405–417.)—The preparation of the sample is the same as that described above. An aliquot portion of the supernatant liquid, after centrifuging, is treated with potassium iodide, and the liberated iodine is titrated with 0·03 N sodium thiosulphate solution, starch paste being used as indicator.

S. G. S.

Tests on Photographic Paper. I. M. Korenman. (*Mikrochem.*, **1936, 21**, 17–20.)—Glossy or semi-matt silver-bromide photographic paper is treated with 10 per cent. sodium thiosulphate to remove the silver salts, and well washed, after which the moist paper is immersed in one of the following reagent solutions and dried. *Solutions.*—(1) For the detection of ferric iron and copper: 10 per cent. solution of potassium ferrocyanide. (2) For the detection of nickel: saturated alcoholic solution of dimethyl glyoxime. (3) For the detection of stannous tin: 1 per cent. gold chloride solution; the test-paper is coloured pale yellow. (4) For the detection of sulphur: saturated solution of lead acetate. (5) For the detection of gold: dilute stannous chloride and pyrogallol solution. (6) For the detection of nitrite: Griess's reagent. *Method.*—A drop of the test solution (0·25 c.mm.) is placed on the reagent paper, where it makes a stain 1 to 1·5 mm. in diameter. When the correct ion is present, the stain rapidly takes on the colour of the reaction product. Although such very small amounts of substance are used, no microscope is necessary, as with reactions in threads. The limits of identification and concentration compared with those of the same test on filter-paper are given below; the reagent solutions are those given above:—

		On filter-paper		On photographic paper	
Ion	Reagent	Limit of identification	Concentration limit	Limit of identification	Concentration limit
$Fe^{\cdot\cdot\cdot}$	1	1γ	1 : 20000	0·0008γ	1 300000
$Cu^{\cdot\cdot}$	1	2γ	1 : 10000	0·0025γ	1 100000
$Ni^{\cdot\cdot}$	2	0·025γ	1 : 800000	0·0003γ	1 800000
S''	4	1·8γ	1 : 11000	0·005γ	1 50000
NO_2'	6	0·015γ	1 : 1300000	0·0002γ	1 1300000
		In threads			
$Sn^{\cdot\cdot}$	3	0·003γ (cotton)	—	0·007γ	1 36000
$Au^{\cdot\cdot\cdot}$	5	0·002γ (silk)	—	0·016γ	1 15600

The nitrite test may be applied to detect nitrous oxide in the atmosphere; as little as 0·2γ per litre may be detected. J. W. M.

Micro-determination of Blood Sugar by Ceric Sulphate Titration. G. Giragossintz, C. Davidson and P. L. Kirk. (*Mikrochem.*, 1936, **21**, 21–34.)—Ferricyanide in alkaline solution is used to oxidise the sugar, and the resulting ferrocyanide is titrated in acid solution with standard ceric sulphate, alphazurine G.G. or phenanthroline ferrous complex being used as indicator. The excess of ferricyanide has no influence on the results and the titration of the ferrocyanide proceeds smoothly to a sharp and reproducible end-point. *Reagent Solutions.*—14 per cent. sodium carbonate solution, made from the anhydrous salt; 3–5 *M* sulphuric acid solution; 0·8 per cent. potassium ferricyanide solution. Standard ceric sulphate solution, preferably about 0·0025 *N*, prepared by the method of Willard and Young (*J. Amer. Chem. Soc.*, 1929, **51**, 149). It is standardised against a weighed sample of potassium ferrocyanide which has been recrystallised and dried. Standard ceric sulphate solution must be kept in a glass bottle, free from organic contamination. *Indicator.*—Either 0·4 per cent. Alphazurine G.G., or 0·025 *M* phenanthroline ferrous complex. *Method.*—The blood is deproteinised in the usual way. Either 2 ml. of the blood filtrate which has been diluted to 1 : 10, or 1 ml. if the dilution was 1 : 5, is pipetted into a large test-tube. To this are added 2 ml. of the ferricyanide solution and 2 ml. of the sodium carbonate solution. A blank solution is also prepared with distilled water in place of the blood filtrate. The tubes are shaken, heated for about 5 minutes on the water-bath, and then cooled, 2 ml. of sulphuric acid are added, followed by a drop of indicator, and the solutions are titrated with the standard ceric sulphate to the end-point, which is a sharp change from yellow to brown with Alphazurine G.G., or from orange to green with phenanthroline. A 10-ml. burette calibrated in divisions of 0·02 ml. is convenient for the titration when 0·0025 N ceric sulphate solution is used. Over the entire range investigated, the same factor holds good, *viz.* 1 mg. of glucose ≡ 2·735 ml. of 0·01 N ceric sulphate solution. The method has been tested in comparison with other methods, and is claimed to be simpler, more readily reproducible and more rapid than those tried, and to give the same value for glucose. J. W. M.

Differentiation of Chromate and Dichromate Ions. M. G. Malko, L. K. Yanowski and W. A. Hynes. (*Mikrochem.*, 1936, **21**, 57–60.)—Hexammino-cobaltic chloride will distinguish between chromate and dichromate ions microscopically in the absence of interfering ions, such as metavanadate, ferrocyanide, ferricyanide, tungstate, molybdate, tetrathionate, ortho- and pyro-phosphate ions. The reagent is a solution of the salt containing 28 g. per litre. Precipitation is carried out at room temperature by mixing one drop of the test solution with two drops of reagent on a slide. With the chromate ion alone, lemon-yellow needles are formed which attain the size of 1 cm. or more, whilst with the dichromate ion the crystals are orange-yellow and microscopic in size, showing a tree-like branching of prisms from a common stalk. Neither crystals resemble those formed on evaporating the reagent. The formula of the chromate precipitate is $(Co[NH_3]_6)(CrO_4)Cl$, and that of the dichromate compound $(Co[NH_3]_6)_2(Cr_2O_7)_3$. On recrystallisation the chlorochromate gives long golden-yellow needles, the dichromate light yellow six-sided or square platelets. With mixtures of chromate and dichromate ions there is a tendency for the precipitation to be retarded and for the chromate needles to be shorter. The proportion limits of the detection of the anions in the presence of each other is $20Cr_2O_7 : 1CrO_4$ and $2{\cdot}5CrO_4 : 1Cr_2O_7$. Two photomicrographs and 4 drawings are given. J. W. M.

Use of Complex Salts for the Detection of Anions. I. Hexammino-cobaltic Chloride. W. A. Hynes and L. K. Yanowski. (*Mikrochem.*, 1937, **23**, 1–9.)—By the use of the reagent and procedure described in the preceding abstract the following ions were found to give characteristic crystalline reaction products when treated with hexammino-cobaltic chloride: bifluoride, bisulphate, bisulphite, chromate, cobaltinitrite, dichromate, dithionate, ferricyanide, ferrocyanide, fluosilicate, iodate, iodide, metavanadate, nitroprusside, orthovanadate, permanganate, persulphate, phosphomolybdate, phosphotungstate, pyrophosphate, sulphate, sulphosalicylate, tartrate, tellurite and thiosulphate. Of these, the following were found to give rapid qualitative tests: bisulphite, chromate, dichromate, dithionate, ferricyanide, ferrocyanide, iodate, permanganate, sulphate, sulphosalicylate and thiosulphate. The cation present in the test substance apparently causes no difference in the crystalline form of the reaction product obtained. The anions react in much the same manner on treatment with the reagent, regardless of whether they are in the form of their salts or occur in solutions containing several anions. Twenty-four photomicrographs are given. J. W. M.

Colorimetric Micro-determination of Manganese. C. P. Sideris. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 445–446.)—Small amounts of manganese (1 to 20γ in 10 ml.) may be determined by the formaldoxime reagent of Denigès (*Compt. rend.*, 1932, 194, 895). The reagent is prepared by dissolving 20 g. of trioxymethylene and 47 g. of hydroxylamine sulphate in 100 ml. of water, by heating. To the slightly acid manganese solution (10 ml.) about 5 drops of 40 per cent. potassium hydroxide solution and 3 drops of the formaldoxime reagent (*cf.* ANALYST, 1934, 59, 200) are added. A wine-red colour immediately develops, and may be compared colorimetrically with that given by a standard manganese solution treated similarly. The amount of manganese in the unknown and standard solutions should be closely similar for accurate results. The addition of a suitable colloid (0·5 ml. of a 5 per cent. solution of gum Ghatti) to the solution prior to the development of the colour is advantageous. Ferric iron, even in traces, interferes by producing a similar red colour. This colour may be prevented from forming by the addition of 0·5 ml. of 20 per cent. sodium cyanide solution to the liquid before adding the formaldoxime. This results, however, in a greenish-yellow colour being formed by the iron, which also interferes, but to a lesser degree. It is necessary, therefore, that the amount of iron present in association with the manganese be determined and added in equal amount to the standard comparison solution. S. G. C.

Reviews

COLLOID CHEMISTRY. By JEROME ALEXANDER, M.Sc. Pp. xviii + 505. London: Chapman & Hall, Ltd. 1937. Price 22s. net.

This is the fourth edition of Mr. Alexander's little book, which first appeared in 1918; it has since been greatly enlarged. The Preface prepares the reader for unusual features. "The author has adhered to the principles which governed the preparation of its predecessors: (1) assemblage of experimental data into naturally co-ordinated and interlocking groups, to form a broad mosaic which gives a coherent picture of nature; (2) breaking down the artificial mental barriers arising from scientific specialisation and its incidental babel of scientific jargon, so that the resources of many fields of investigation may be considered and both breadth and depth of mental focus acquired."

"The book is built around no one theory." It is so arranged that emphasis is placed on observable facts, the theoretical considerations being incidentally invoked for a better appreciation. The author claims that his book should appeal to the student and to the general reader. "The attempt is made to humanise the bare skeleton of scientific principles by using numerous practical illustrations, so that interest may aid memory and knowledge be painlessly acquired."

There is the Sunday School anecdote (p. 110); the French at Verdun: "They shall not pass!" (p. 121); the church raffle (p. 123); collapsed saponin foam films remain after bubble collapse, "like the grin of the Cheshire cat" (p. 75); ten million cornets playing *fortissimo* emit one horse-power of sound (p. 43); "grandma's copper preserving kettle" (p. 50); the "peck of dirt" we acquire in our lifetime (p. 50); these, and many others, certainly give this book a peculiar interest. When also one realises that zip fasteners, relativity, quantum mechanics and chain reactions all meet with the same racy treatment, and the author speaks of "slow movies" or "water won't wet oil," the difficulty of properly assessing the merit and utility of the book becomes obvious.

The twenty-four chapters embrace an astonishing range of subjects, and references are frequent to the author's well-known four volumes on Colloid Chemistry. Indeed, in a sense, the present volume is an epitome of the larger volumes which Mr. Alexander edited. There is a chapter on genetics, one on hormones, another on physiology and pathology, and one on bio-electricity. Some sections, for example that on meteorology, are unusually arresting to the reader.

Among several errors noted are, on p. 213, the "British" Mayonnaise Manufacturers' Association should read "American"; "dynes per sq. cm." (p. 103) is unpardonable; Pbs (p. 80); Jordan and Falk's book is wrongly titled (p. 128).

The reviewer has read this book with very real pleasure and interest, but he cannot recommend it as a *text-book* for students. The treatment is far too cursory—in fact, scrappy, on the basic principles. To anyone already familiar with a modern text-book on the subject, the volume can be recommended as very entertaining reading, and as a guide to more thorough sources of information on the many aspects of knowledge which involve colloid science in their fuller development. WILLIAM CLAYTON

REAGENT CHEMICALS AND STANDARDS. By JOSEPH ROSIN. Pp. x + 530. London: Chapman & Hall. 1937. Price 30s. net.

This book contains methods for testing and assaying 474 different reagent chemicals, together with standards and limits of impurities. The author is chief chemist to Merck & Co. in the United States, and is thus well qualified to write on this subject. It is certainly the most comprehensive work on chemical reagents that has yet been published. The monographs are arranged in alphabetical order, and under each heading are given the formula, molecular weight, theoretical percentages of the constituent elements or groups, appearance and solubility. Then follow the standards, methods of assaying, and of testing for impurities. All the descriptions are highly compressed, and everything has been done to save type. As an illustration of the style we may quote from potassium bromide. "Sulfate: Dissolve 4 g in 25 cc of H_2O, add 1 cc of 1 *N* HCl and 2 cc of $BaCl_2$. Any resulting turbidity is not more than in a blank to which 0·2 mg of SO_4 has been added."

The book is, in fact, a laboratory methods book containing the essential details for carrying out the tests expressed in the shortest possible form. Its practical value is, of course, not less for this reason. One very useful feature is the inclusion of the logarithms beside all chemical factors.

Free use has been made of the tests and standards prescribed by the Committee on Analytical Reagents of the American Chemical Society, though these have been improved in many instances.

The mass of material contained in the book makes it impossible to criticise it in detail, but the following are a few points which have been noted. There is no test for fluorides in phosphates—a notable omission. There is no mention of lead as an impurity in iron salts, though it is often present in serious amount. It is not clear on what principle arsenic tests are included. There are none, for example, for citrates, tartrates, or any iron salts except ferric chloride. It is rather surprising to find that the tests for reagent chloroform are less stringent than those of the British Pharmacopoeia.

At the end of the book are 38 pages containing in considerable detail methods for the preparation of volumetric solutions, and a most comprehensive list of equivalents and their logarithms. There is also a useful section on pH determinations.

Fortunately in these days it is rarely necessary for the analyst to test his own reagents. Nevertheless there are occasions when it is essential to do so, and at such times this book will be found extremely useful. It is also of great value as an indication of what impurities are likely to occur in individual chemicals. The printing is admirable, and not a single misprint has been detected.

NORMAN EVERS

DAS WASSERSTOFFPEROXYD UND DIE PERVERBINDUNGEN. By W. MACHU. Pp. 408. Vienna: Julius Springer. 1937. Price RM.39.

In this volume are collected details of the preparation, properties, chemistry and uses of hydrogen peroxide, the metallic peroxides, the organic peroxides, the per-acids and the per-salts. These substances are finding increased application in industry, medicine and the household, and in this connection the voluminous data collected should be very valuable.

For over 100 years the only process for preparing hydrogen peroxide was from barium peroxide, the product being an impure solution with a maximum strength of about 5 per cent. This process is still carried on, but exists only because there is a market for the by-product, barium sulphate. At the present time 80 per cent. of the supply is made by three electrical processes, the usual strength of the product being 30 per cent. (100 volumes), but it may be higher. During the last twenty years the employment of distillation processes for concentrating dilute solutions of hydrogen peroxide up to the anhydrous article has yielded products of such strength and purity that the chemistry of the peroxides has been developed in a way impossible when hydrogen peroxide was only known as an impure solution. During the same period the development of electrochemical processes has brought the per-compounds from curiosities to household articles.

From many points of view molecular oxygen may be regarded as an unsaturated unit capable of forming addition products. The —O—O— linkage may be saturated with hydrogen, with metals or with organic radicals. In the oxidation of organic substances with oxygen, peroxides are always formed as intermediate products, although they may not always be stable. This is important in determining the mechanism of biological processes involving oxidation. An example, which is perhaps outside the purview of this book, is the production of aroma in butter, which is due to peroxides; and whether or not the diacetyl and acetyl-methyl-carbinol are produced, as has been suggested, from citric acid, their formation appears to be closely associated with the presence of oleic peroxide. The use of anti-oxidants is increasing, and although many of them are of a non-reducing character, it is probable that they are capable of removing or decomposing peroxides under the particular conditions obtaining at the moment of their formation. Oxidases, peroxidases and catalases, which also have the power of decomposing peroxides, are widespread in nature.

Organic peroxides are important not only to oxidation processes in which they are essential intermediates, but also to many reactions promoted by their formation or decomposition. As a result of recent work, subsequent to the data here recorded, it has been shown that peroxides may control the velocity and orientation of reaction between hydrogen bromide and olefines, and the exceptions to Markownikoff's rules, which have been a mystery since 1870, are now largely explained. It has also recently been shown that in the absence of peroxides, benzaldehyde does not undergo the Cannizzaro reaction.

The book is well printed but, unfortunately, is uncut. Over 100 feet of paper have to be slit piecemeal before all the letterpress is available. A few minor misprints have been noted, such as "benzoperoxyd" (p. 80), "koovalenten" (p. 81), and "benzyl" for "benzoyl" on two occasions (p. 394); an error occurs in the lettering of the figure on p. 173. There are few English or American references since 1930, and as a result some recent work finds no place. The suggestion to use organic solvents for dissolving such organic peroxides as are insoluble in water prior to iodimetric determination is not of general application, for in some instances the solvent is oxidised.

The value of the book to certain technical specialists is undoubted. But the pure organic chemist or biochemist may find it of increasing and possibly unsuspected interest; for it may fairly be said that the part played by peroxides and allied compounds, either directly or indirectly, in many reactions is only beginning to be appreciated.

J. R. NICHOLLS

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 3rd, 1937, the President, Dr. G. Roche Lynch, in the chair.

Certificates were read in favour of:—Harold Firth Bamford, B.A., Cecil Robertson Bond, M.Sc.Tech., F.I.C., Frederic Alan Dawson, B.Sc., John Hawthorne, B.A., Ph.D., F.I.C., Geoffrey Moses, A.M.C.T., F.I.C., Marcus Robinson, B.Sc., A.I.C., and John Linley Wilson, M.Sc., F.I.C.

Miss Mabel Beatrice Elliott, M.B.E., was elected an Honorary Member of the Society.

The following were elected Ordinary Members:—Donald Colin Malcolm Adamson, A.I.C., B. Boas, B.Sc., Ernest Oddy, Gerald Lionel Ransome, B.Sc., A.I.C., and Reginald Frank Wright, B.Sc., A.R.C.S., F.I.C.

The following papers and report were presented:—"The Ascorbic Acid Content of Fruits and Vegetables," by Mamie Olliver, M.Sc., A.I.C.; "World's Dairy Congress," Report by W. L. Davies, Ph.D., M.Sc., F.I.C.; "A Method for the Routine Determination of Glycogen in Oysters," by John P. Tully (Ministry of Fisheries, Canada).

NORTH OF ENGLAND SECTION

A meeting of the above Section was held in Manchester on Saturday, October 30th. The Chairman (Mr. A. R. Tankard) presided over an attendance of forty-nine, which included the President (Dr. G. Roche Lynch).

The following paper was read and discussed:—"The Evolution of the Public Analyst," by E. Gabriel Jones, M.Sc., F.I.C.

A discussion on the "Misdescription of Foods and Drugs" was introduced by the Chairman, and many members took part.

The Examination of Ginger

By G. D. ELSDON D.Sc., F.I.C., and CATHERINE MAYNE, B.Sc.,
A.M.C.T., A.I.C.

(Read at the Meeting of the North of England Section, December 8th, **1934***)*

The composition of exhausted ginger will depend to a very large extent on the process to which it has been subjected; extraction with alcohol, as for the tincture, leads to a low alcoholic extract, whilst extraction with water or dilute alcohol, as in the preparation of ginger ale, will lead to low figures for soluble ash and aqueous extract. As no recent figures have been published for commercial exhausted gingers prepared in this country, we have examined a considerable number, with the results given in Tables I and II.

TABLE I

COMPOSITION OF EXHAUSTED GINGERS FROM TINCTURES, ETC.

No. of sample	Source	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.	Ether ext.			Loss at 100° C. Per Cent.	Fibre Per Cent.
							Total Per Cent.	Volatile Per Cent.	Fixed Per Cent.		
7042	Jamaica	4·0	2·9	0·2	15·4	0·5	0·3	0	0·3	10·4	3·2
7043	,,	3·7	2·7	0·2	15·9	0·2	0·3	0·1	0·2	10·9	3·6
7050	,,	3·5	2·5	0·2	15·1	0·7	0·7	0·1	0·6	11·3	3·5
7052	,,	3·8	2·8	0·1	15·2	2·2	2·3	0·7	1·6	11·6	3·4
7055	,,	4·4	3·4	0·2	10·1	0·4	0·3	0	0·3	8·6	3·8
7048	Africa	5·5	2·5	1·0	0·8	4·5	4·2	0·4	3·8	9·9	4·9
7054	,,	6·2	2·7	1·2	11·7	2·2	2·2	0·2	2·0	9·1	5·7
7041	Calicut	8·2	3·2	1·4	15·8	3·7	3·8	0·3	3·5	8·2	9·2
7047	,,	9·9	2·8	2·4	12·3	0·6	0·7	0·2	0·5	9·5	9·1
7056	,,	2·9	1·6	0·2	7·5	0·3	0·2	0	0·2	10·5	4·5

TABLE II

COMPOSITION OF EXHAUSTED GINGERS FROM GINGER-BEER, ETC.

No. of sample	Source	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.	Ether ext.			Loss at 100° C. Per Cent.	Fibre Per Cent.
							Total Per Cent.	Volatile Per Cent.	Fixed Per Cent.		
7046	Jamaica	2·2	1·3	0·2	10·8	3·0	4·0	1·3	2·7	14·4	3·3
7053	,,	3·5	2·3	0·2	2·7	2·3	2·9	0·8	2·1	13·2	4·2
7049	Africa	1·9	0·4	0·3	4·7	3·4	4·8	1·4	3·4	13·8	5·9

A number of authenticated whole gingers from various sources have also been examined. These were ground in the laboratory, and, on examination, gave results shown in Table III.

The present investigation was commenced after the receipt under the Food and Drugs Act of a sample of ground ginger with the following characteristics:—total ash, 2·96; soluble ash, 2·34; alcoholic extract, 3·6; aqueous extract, 14·8 per cent.

This alcoholic extract is considerably less than the figure of 4·5 per cent. suggested in the 1932 revision of the British Pharmacopoeia (XI) as a minimum; in

TABLE III

UNEXHAUSTED GINGERS

No. of sample	Source	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.	Ether ext.			Loss at 100° C. Per Cent.	Fibre Per Cent.
							Total Per Cent.	Volatile Per Cent.	Fixed Per Cent.		
7016	Jamaica	3·8	2·5	0·4	16·8	6·9	—	—	—	—	—
7018	,,	3·3	2·4	0·2	16·2	4·1	4·1	0·9	3·2	11·4	2·3
7019	,,	4·0	3·0	0·2	15·8	3·0	3·8	1·0	2·8	12·5	3·0
7022	,,	3·3	2·5	0·2	14·2	3·6	4·0	1·2	2·8	11·5	2·0
7028	,,	3·2	2·6	0·1	14·6	3·1	3·9	0·9	3·0	11·1	2·6
7031	,,	3·5	2·8	0·0	14·7	3·4	4·5	1·2	3·3	11·3	3·5
7032	,,	4·1	3·3	0·1	18·0	3·4	4·5	1·3	3·2	11·2	3·4
7044	,,	3·5	2·6	0·2	17·1	3·6	3·8	0·8	3·0	12·3	2·7
7045	,,	3·6	2·6	0·3	16·6	3·9	4·5	1·2	3·3	13·6	2·9
7051	,,	3·2	2·0	0·1	13·9	3·7	4·2	1·6	2·6	12·8	4·3
7020	Africa	5·0	2·1	0·6	12·1	6·2	7·1	1·6	5·5	12·0	5·3
7021	,,	4·1	2·3	0·6	13·8	6·9	6·9	1·9	5·0	13·4	4·5
7023	,,	4·3	2·4	0·6	13·0	5·8	6·8	2·0	4·8	11·7	4·5
7026	,,	4·0	1·8	0·9	11·3	4·9	6·6	2·0	4·6	13·2	4·3
7027	,,	2·9	1·5	0·3	11·4	5·7	7·4	2·3	5·1	10·6	4·1
7030	,,	4·2	2·7	0·3	12·2	5·5	7·6	2·1	5·5	11·6	4·4
7033	,,	3·7	2·3	0·1	9·9	5·3	7·4	2·4	5·0	12·8	4·9
7017	Cochin	3·9	2·6	0·3	13·5	4·6	5·7	1·5	4·2	—	—
7024	,,	2·8	1·5	0·2	9·5	5·1	6·5	2·0	4·5	13·0	5·3
7029	,,	4·7	2·5	0·2	10·6	4·1	5·6	1·6	4·0	11·6	2·9
7035	,,	5·0	3·1	0·3	12·5	3·9	5·6	1·8	3·8	12·5	4·3
7036	,,	5·0	3·2	0·4	11·9	4·8	6·4	1·9	4·5	11·4	4·7
7034	Cuttings	6·3	3·2	0·6	15·7	8·4	11·0	3·6	7·4	13·3	7·9
7037	,,	6·6	2·7	0·9	16·3	7·2	8·7	2·7	6·0	12·4	9·4

fact, it was the lowest figure which had, up to that time, come within our personal experience. The firm supplying this article willingly supplied further samples of their ground ginger together with the whole gingers from which these were obtained. The whole gingers were ground in the laboratory, and the constants were determined, with the following results:—

TABLE IV

Source	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Alcohol ext. Per Cent.	Water ext. Per Cent.
*Original sample ..	3·0	2·3	—	3·6	14·7
Whole Jamaica ..	3·8	2·4	0·4	6·8	16·8
†Ground Jamaica ..	3·7	2·1	0·1	3·9	14·9
Whole Cochin ..	3·9	2·6	0·3	4·6	13·5
†Ground Cochin ..	4·1	2·1	0·1	4·2	14·6

* Three months later the alcoholic extract of this sample was 3·1 and the aqueous extract 14·8 per cent. † As submitted.

It is obvious that this particular firm is making use of ground gingers giving alcoholic extracts much below the average, and it became of interest to discover, if possible, how far these low alcoholic extracts were due to the composition of the original ginger and how far they were due to the mechanical separation of the coarser outer portions, which might contain far more material soluble in alcohol.

In order to discover what differences in the amount of alcohol-soluble matter are to be expected in different parts of the ginger root, a specimen of whole Jamaica ginger (scraped; unscraped ginger is not exported from Jamaica) was cut into three portions, consisting respectively of the outer skin, a harder intermediate portion of resinous appearance, and a softer fibrous inner portion. Each portion was examined separately, with the following results:

TABLE V

DIFFERENT PORTIONS OF THE SAME GINGER

Portion	Percentage of whole	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.
Outer ..	41·1	3·9	2·7	0·2	16·0	8·1
Middle ..	28·1	3·5	3·0	0·1	16·6	5·0
Inner ..	30·8	3·5	3·0	0·1	13·3	4·5

These results suggested that low results for alcoholic extract might be accounted for by the rejection of the outer darker layers during grinding, in order that a lighter product might be produced after grinding. In order to test this suggestion all the root gingers given in Table III were divided into two portions (there appeared to be no object in separating the internal, apparently resinous, layer from the fibrous), and each portion was examined. The following results were obtained:

TABLE VI

JAMAICA GINGER: EXAMINATION OF OUTER AND INNER PORTIONS

No. of sample	Portion	Percentage of whole	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.	Ether ext. Total Per Cent.	Ether ext. Volatile Per Cent.	Ether ext. Fixed Per Cent.	Loss at 100° C. Per Cent.	Fibre Per Cent.
7019	Outer	33·5	4·2	3·0	0·2	15·2	4·4	5·5	1·6	3·9	12·3	3·8
	Inner	66·5	3·9	3·1	0·2	16·1	2·4	3·0	0·8	2·2	12·6	2·6
7028	Outer	30·4	3·6	2·7	0·1	13·7	4·5	5·7	1·4	4·3	11·3	3·3
	Inner	69·6	3·0	2·4	0·1	15·0	2·5	3·2	0·7	2·5	11·0	2·3
7031	Outer	34·1	4·0	3·1	0·0	15·1	5·0	6·7	2·0	4·7	11·1	4·7
	Inner	65·9	3·3	2·7	0·0	14·5	2·5	3·4	0·9	2·5	11·4	3·0
7032	Outer	33·8	4·2	3·3	0·1	17·2	4·7	6·4	2·0	4·4	10·7	4·6
	Inner	66·2	4·0	3·2	0·1	18·5	2·8	3·5	0·9	2·6	11·5	2·8

TABLE VII

AFRICAN GINGER: EXAMINATION OF OUTER AND INNER PORTIONS

No. of sample	Portion	Percentage of whole	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.	Ether ext. Total Per Cent.	Ether ext. Volatile Per Cent.	Ether ext. Fixed Per Cent.	Loss at 100° C. Per Cent.	Fibre Per Cent.
7021	Outer	38·1	6·1	2·3	1·4	13·9	7·9	10·2	3·1	7·1	13·7	8·2
	Inner	61·9	2·8	2·2	0·1	13·8	4·0	4·9	1·3	3·6	12·9	2·2
7026	Outer	49·2	5·4	1·8	1·7	10·8	6·5	9·2	3·0	6·2	14·3	6·9
	Inner	50·8	2·6	1·8	0·2	11·8	3·5	4·2	1·1	3·1	12·2	1·9
7027	Outer	43·6	3·7	1·4	0·5	10·5	7·4	9·7	3·2	6·5	10·6	5·9
	Inner	56·4	2·3	1·5	0·1	12·0	3·4	4·5	1·3	3·2	10·6	2·1
7030	Outer	46·7	5·4	2·9	0·6	12·5	7·6	10·8	3·2	7·6	12·2	6·5
	Inner	53·3	3·1	2·4	0·1	11·9	3·7	4·7	1·2	3·5	11·2	2·1
7033	Outer	32·7	6·0	2·4	0·1	10·7	9·1	13·0	4·5	8·5	13·6	9·6
	Inner	67·3	2·6	2·1	0·1	9·5	3·4	4·8	1·4	3·4	11·6	2·6

TABLE VIII

COCHIN GINGER: EXAMINATION OF OUTER AND INNER PORTIONS

No. of sample	Portion	Percentage of whole	Total ash Per Cent.	Sol. ash Per Cent.	Sand Per Cent.	Water ext. Per Cent.	Alcohol ext. Per Cent.	Ether ext.			Loss at 100° C. Per Cent.	Fibre Per Cent.
								Total Per Cent.	Volatile Per Cent.	Fixed Per Cent.		
7017	Outer	43·3	5·2	3·1	0·5	15·2	6·9	9·4	2·4	7·0	—	—
	Inner	56·7	2·8	2·2	0·1	12·2	2·9	2·8	0·7	2·1	—	—
7024	Outer	39·6	4·0	1·3	0·5	9·7	8·2	11·0	3·4	7·6	13·3	9·3
	Inner	60·4	2·0	1·4	0·1	9·4	3·0	3·6	1·0	2·6	12·9	2·6
7029	Outer	39·4	7·4	3·6	0·3	12·2	6·0	8·4	2·6	5·8	12·2	4·8
	Inner	60·6	3·0	1·7	0·1	9·6	2·9	3·8	1·0	2·8	11·3	1·6
7035	Outer	36·4	7·4	3·1	0·8	13·5	6·5	9·6	3·2	6·4	12·8	7·7
	Inner	63·6	3·6	3·0	0·0	12·0	2·5	3·5	1·0	2·5	12·4	2·4
7036	Outer	33·0	6·2	2·0	0·9	12·8	8·1	11·2	3·6	7·6	12·6	9·1
	Inner hard	34·8	3·0	2·2	0·1	13·2	3·1	4·0	1·2	2·8	10·6	2·7
	Inner soft	32·3	6·0	5·4	0·2	9·6	3·2	4·1	1·0	3·1	11·0	2·3

From the results given in Tables VI, VII and VIII, it is quite obvious that the outer portions of whole ginger contain very different proportions of alcohol-soluble and ether-soluble matters from those contained in the inner portions, and that an opinion based merely upon a determination of these values may not decide between a ginger partially exhausted by solvent and one that has been separated by mechanical means. This at once raises the question whether such mechanical separation is legitimate. Before this can be answered a decision must be reached as to which portion of the ginger is the one desired, but it would appear that if this be the pungent resin or the aromatic volatile oil, the outer skin is by far the better source. It has not been possible (on account of Jamaican law) to obtain uncut Jamaica ginger, but it would appear reasonable to suppose that the low values usually obtained for the alcoholic extract of Jamaica ginger are partially due to the decortication which it undergoes. From the footnote to Table IV it would appear that there is a considerable loss in alcoholic extract on keeping. Another sample of ground ginger changed in alcoholic extract from 6·6 to 5·6 per cent. when kept for four and a half months in a glass jar having a metal screw top.

It is not easy to distinguish a ginger which is low in alcoholic extract owing to natural causes or to removal of some portion of the outer coating, from one which is deficient owing to the presence of exhausted ginger. Microscopical examination may be of some assistance, but out of thirteen samples of exhausted ginger mentioned above, only three showed gelatinised starch granules. In the others the starch granules were cleaner than in genuine samples, and there were varying amounts of broken granules and some cell débris. In the absence of gelatinised starch grains it would scarcely be possible to distinguish, with absolute certainty, a genuine from an exhausted ginger by microscopical means, and the detection of small admixtures would be impossible.

Where, however, the low alcoholic extract is due to natural causes it is usual to find a high water-soluble extract, because Jamaica ginger is the type of ginger showing the lowest alcoholic extract. The fibre, too, should be on the low side, because the fibre-content of the inner portions of the root is much less than that of the outer portions.

It may be assumed that any ginger having an alcoholic extract less than 3·0 per cent. is adulterated. One with an alcoholic extract between 3·0 per cent. and 4·5 per cent. may be genuine, but the fibre should then be low (less than about 3·0 per cent.), and the aqueous extract not less than about 12·0 per cent.

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LANCASHIRE COUNTY LABORATORY
COUNTY OFFICES, PRESTON

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Analysis of Coffee Infusions

By F. W. EDWARDS, F.I.C., and H. R. NANJI, Ph.D., D.I.C., F.I.C.

(*Read at the Meeting, October 6, 1937*)

The analysis of coffee in the ground state presents few difficulties, but the examination of coffee infusions, as served in restaurants and elsewhere, is by no means so simple and does not appear to have been seriously considered by Public Analysts; or perhaps it would be nearer the truth to say that they have been repelled by the numerous difficulties of the task and the apathy of their authorities. For throughout a diligent search of the literature we found no direct reference to this subject, although some work was published by Tatlock and Thomson[1] on the analysis and composition of coffee, chicory, and coffee and chicory "essences," and a few communications have appeared recently on the analysis of coffee and chicory, with particular reference to the extractives (*cf.* Hughes and Wise,[2] Dyer,[3] Bunce and Moitra[4] and others) which formed the basis of a discussion on related subjects at a Joint Meeting of this Society with the Food Group of the Society of Chemical Industry.[5]

Moreover, the law with regard to the sale of coffee mixtures and coffee extracts is at present far from satisfactory, for almost any percentage of chicory may be present and the possibility of a successful issue to a prosecution is somewhat remote. In our experience, many coffee and chicory mixtures, containing usually over sixty per cent. of chicory, are sold with impunity as "French Coffee." But this appellation has no meaning in France itself, and it is significant that official replies to enquiries made recently laid stress upon this fact; from accompanying references to French law* relating to the subject it is plain that the sale of coffee mixed with any such ingredient as chicory is prohibited. Precise Regulations also exist in some Dominions; in Canada coffee mixtures must be labelled as such, and the names and proportions of ingredients must be stated on the label. In South Africa mixtures of ground coffee and chicory must contain a minimum of 75 per cent. of coffee. Considering the analytical and legal difficulties involved, it is not at all surprising that local authorities at home have devoted so little attention to adulteration of coffee infusions.

During a study of the subject in all its aspects we sought for methods of solving the chemical side of the problem and submitted such as seemed to promise success to as thorough an investigation as possible. We found that the only actual determinations necessary in routine work are those of extractives, ash, chloroform extract and caffeine, though it should be obvious that for certain products others may be needed; for example, in sweetened decoctions the sugars may have to be determined. The analytical methods adopted are detailed later in this communication.

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* A presidential decree of the 7th of October, 1932, states that:

"It is prohibited to hold in stock, to sell or re-sell under the name of 'coffee,' with or without sub-titles, or under a denomination which includes the word 'coffee,' or a word derived from the same, any products other than the bean of the coffee plant, which must not have been subjected to any treatment other than roasting."

"It is prohibited to stock, sell or re-sell under the name 'chicory,' with or without sub-title, any product other than the root of the chicory plant properly cleaned, roasted and ground."

In our preliminary work the anticipation proved to be correct—that the ratios of extractives to caffeine, extractives to ash, extractives to chloroform extract, ash to caffeine, and ash to chloroform extract would lie within certain narrow limits for pure coffee, and it was found possible to detect adulteration, and even to determine its amount, by the proper use of these ratios. It was necessary to examine coffees of different origin—Brazil, Costa Rica, India, Kenya, Mocha, Mysore and Tanganyika—and of different degrees of roasting, as well as to determine the effect upon the analytical results of different methods of preparing the coffee infusions, because such conditions as prolonged heating or simmering might alter the amount of caffeine and other constituents.

Accordingly, decoctions were prepared from coffees of different origin and different degrees of roasting in five ways, with a view to determining if all or any of these variations had any effect on the value of the ratios. The following methods of preparing the decoction in the laboratory were adopted:

(A) By extracting from 5 g. of the coffee the total water-soluble matter by the method of Jones.[6]

(B) By adding 300 ml. of boiling water to 5 g. of coffee and keeping for 5 minutes, with occasional stirring, and then straining off the liquor.

(C) As in (B), but using double the amount of coffee.

(D) By adding 300 ml. of boiling water to 5 g. of coffee and "refluxing" on a steam-bath for 4 hours, with occasional shaking, and then straining off.

(E) By adding 300 ml. of boiling water to 5 g. of coffee and simmering on a gas burner for 10 minutes, finally adjusting the volume to the original and straining.

The infusions obtained are weak, perhaps only a half or a third of the strength of those made in the home or in restaurants. In other series of experiments, quoted later, stronger infusions were employed. The results obtained, together with the ratios calculated therefrom, are given in Tables I to VI. The letters in the heading of these tables identify the figures with the above-mentioned methods of preparing the infusion.

TABLE I

SAMPLE NO. 1—ORDINARY ROAST

		A	B	C	D	E
Extractives	per cent. . .	0·484	0·356	0·734	0·470	0·430
Ash	,, ,, . .	0·085	0·071	0·139	0·082	0·079
Chloroform extract	,, ,, . .	0·055	0·035	0·065	0·041	0·059
Caffeine	,, ,, . .	0·030	0·027	0·047	0·027	0·028
Ratios :						
Extractives to caffeine . .	. .	16·1 /1	12·9 /1	15·6 /1	17·3 /1	15·3 /1
Extractives to ash . .	. .	5·7 /1	5·0 /1	5·3 /1	5·7 /1	5·4 /1
Ash to caffeine . .	. .	2·83/1	2·57/1	2·96/1	3·02/1	2·80/1
Extractives to chloroform extract		8·8 /1	10·2 /1	11·3 /1	9·1 /1	7·3 /1
Ash to chloroform extract	. .	1·55/1	2·03/1	2·14/1	2·0 /1	1·34/1

TABLE II

SAMPLE NO. 2—ORDINARY ROAST

		A	B	C	D	E
Extractives	per cent. ..	0·498	0·348	0·722	0·462	0·446
Ash	„ „ ..	0·080	0·065	0·120	0·073	0·072
Chloroform extract	„ „ ..	0·056	0·036	0·094	0·041	0·055
Caffeine	„ „ ..	0·029	0·025	0·044	0·024	0·025
Ratios :						
Extractives to caffeine ..	..	17·1 /1	13·9 /1	16·4 /1	19·2 /1	17·8 /1
Extractives to ash	.. ..	6·2 /1	5·3 /1	6·0 /1	6·3 /1	6·2 /1
Ash to caffeine ..	.. ..	2·76/1	2·60/1	2·73/1	3·04/1	2·88/1
Extractives to chloroform extract		8·9 /1	9·7 /1	7·7 /1	11·3 /1	8·1 /1
Ash to chloroform extract	..	1·43/1	1·80/1	1·28/1	1·78/1	1·30/1

TABLE III

SAMPLE NO. 3—ORDINARY ROAST

		A	B	C	D	E
Extractives	per cent. ..	0·472	0·344	0·684	0·458	0·408
Ash	„ „ ..	0·076	0·066	0·113	0·070	0·069
Chloroform extract	„ „ ..	0·052	0·045	0·079	0·043	0·052
Caffeine	„ „ ..	0·028	0·025	0·043	0·024	0·024
Ratios :						
Extractives to caffeine ..	..	16·8 /1	13·8 /1	15·9 /1	19·1 /1	17·0 /1
Extractives to ash	.. ..	6·2 /1	5·2 /1	6·0 /1	6·5 /1	5·9 /1
Ash to caffeine ..	.. ..	2·71/1	2·60/1	2·63/1	2·92/1	2·90/1
Extractives to chloroform extract		9·0 /1	7·6 /1	8·7 /1	10·6 /1	7·8 /1
Ash to chloroform extract	..	1·46/1	1·44/1	1·43/1	1·63/1	1·30/1

TABLE IV

SAMPLE NO. 4—HIGH ROAST

		A	B	C	D	E
Extractives	per cent. ..	0·540	0·392	0·794	0·510	0·464
Ash	„ „ ..	0·090	0·072	0·135	0·085	0·081
Chloroform extract	„ „ ..	0·070	0·051	0·100	0·050	0·084
Caffeine	„ „ ..	0·030	0·028	0·050	0·028	0·029
Ratios :						
Extractives to caffeine ..	..	17·7 /1	14·0 /1	15·9 /1	18·2 /1	16·0 /1
Extractives to ash	.. ..	6·0 /1	5·4 /1	5·9 /1	6·0 /1	5·7 /1
Ash to caffeine ..	.. ..	2·95/1	2·60/1	2·70/1	3·04/1	2·80/1
Extractives to chloroform extract		7·7 /1	7·7 /1	7·9 /1	10·2 /1	5·5 /1
Ash to chloroform extract	..	1·28/1	1·41/1	1·35/1	1·70/1	0·96/1

TABLE V

SAMPLE NO. 5—HIGH ROAST

		A	B	C	D	E
Extractives	per cent. ..	0·538	0·396	0·778	0·504	0·464
Ash	„ „ ..	0·084	0·070	0·130	0·079	0·075
Chloroform extract	„ „ ..	0·074	0·048	0·115	0·057	0·098
Caffeine	„ „ ..	0·028	0·024	0·044	0·026	0·026
Ratios :						
Extractives to caffeine ..	..	19·2 /1	16·5 /1	17·7 /1	19·4 /1	17·8 /1
Extractives to ash	.. ..	6·4 /1	5·6 /1	6·0 /1	6·4 /1	6·2 /1
Ash to caffeine ..	.. ..	3·0 /1	2·90/1	2·95/1	3·04/1	2·90/1
Extractives to chloroform extract		7·3 /1	8·2 /1	6·8 /1	8·8 /1	4·7 /1
Ash to chloroform extract	..	1·14/1	1·45/1	1·13/1	1·39/1	0·76/1

TABLE VI

SAMPLE NO. 6—HIGH ROAST

		A	B	C	D	E
Extractives	per cent. . .	0·530	0·394	0·782	0·516	0·462
Ash	,, ,, . .	0·084	0·070	0·129	0·075	0·073
Chloroform extract	,, ,, . .	0·069	0·057	0·091	0·054	0·082
Caffeine	,, ,, . .	0·028	0·026	0·044	0·025	0·026
Ratios :						
Extractives to caffeine . .	. .	18·9 /1	15·2 /1	17·8 /1	20·6 /1	17·7 /1
Extractives to ash . .	. .	6·3 /1	5·6 /1	6·1 /1	6·9 /1	6·3 /1
Ash to caffeine . .	. .	3·0 /1	2·7 /1	2·93/1	3·0 /1	2·8 /1
Extractives to chloroform extract		7·7 /1	6·9 /1	8·6 /1	9·5 /1	5·6 /1
Ash to chloroform extract	. .	1·21/1	1·23/1	1·42/1	1·39/1	0·89/1

It will be seen that, in spite of the fact that the decoctions were prepared in different ways—some mild and others rather drastic—from a representative range of samples, the three ratios of extractives to caffeine, extractives to ash, and ash to caffeine do not exceed certain limits.

The ratio of extractives to caffeine, so far as our results indicate, does not exceed about 20 to 1, the limits being 12·9 to 1 and 20·6 to 1. In decoctions prepared by the rather drastic method of heating for 4 hours the ratio approaches the upper limiting value, mainly because a little caffeine is destroyed by the prolonged heating. Therefore, if the ratio exceeds 20 to 1, adulteration is indicated, and if it exceeds, say, 24 to 1, there can be little doubt of admixture with chicory or some other adulterant.

The ratio of extractives to ash is about 6 to 1, and a limiting value of 7 to 1 is probably a reasonable one to adopt. If, therefore, the actual extractives found exceed seven times the ash, chicory or some other adulterant is definitely indicated. It is important to bear in mind that this ratio is of particular use in the examination of partly or wholly de-caffeinised coffee, as it is almost unaffected by the removal of caffeine. Further work on this type of coffee is in progress; the results already obtained show that with such coffee only the caffeine figure is altered, the other figures being normal.

The ratio of ash to caffeine fluctuates within the narrow limits of 2·57 to 1 and 3·04 to 1, and we suggest a generous limit of 4 to 1, a higher ratio being taken to indicate adulteration. This ratio is of special importance in the examination of sweetened coffee liquor, as it will not be appreciably affected by the presence of the added sugar.

The two ratios of extractives to chloroform extract and of ash to chloroform extract are not so useful as was originally anticipated, because the chloroform extract appears to vary rather considerably according to the degree of roasting and the method of preparing the decoction.

Tatlock and Thomson[1] express the opinion that the caffeine and mineral matter bear the same relationship to the total water extract, whether the coffee is fully or only partly exhausted. They did not give any details of their experiments in this direction, nor did they quote any figures; moreover, the effects of roasting and the method of preparing the infusion were apparently not considered.

We have examined, on the lines indicated, a number of coffees submitted under the Food and Drugs Act. The results in Table VII are those obtained with 2 per cent. solutions prepared by complete extraction of the solid samples with water.[6] The last sample (No. 7) was sold as a mixture of coffee and chicory; the results obtained indicate in a striking manner the utility of the three ratios as evidence of adulteration.

TABLE VII

SAMPLES OF COFFEE, ETC., RECEIVED UNDER THE FOOD AND DRUGS ACT

	1	2	3	4	5	6	7
Extractives, per cent.	0·506	0·494	0·506	0·508	0·530	0·558	0·900
Ash ,, ,,	0·076	0·081	0·078	0·077	0·082	0·080	0·078
Chloroform extract per cent.	0·060	0·065	0·071	0·090	0·072	0·119	0·038
Caffeine ,, ,,	0·026	0·024	0·027	0·026	0·025	0·028	0·016
Ratios :							
Extractives to caffeine	19·3 /1	20·8 /1	19·0 /1	19·7 /1	21·0 /1	19·9 /1	56·0 /1
Extractives to ash ..	6·7 /1	6·1 /1	6·5 /1	6·6 /1	6·5 /1	7·0 /1	11·5 /1
Ash to caffeine ..	2·9 /1	3·4 /1	2·92/1	3·0 /1	3·25/1	2·86/1	4·87/1
Extractives to chloroform extract ..	8·4 /1	7·6 /1	7·1 /1	5·6 /1	7·3 /1	4·7 /1	23·7 /1
Ash to chloroform extract	1·26/1	1·20/1	1·10/1	0·86/1	1·14/1	0·67/1	2·0 /1

It would seem justifiable to assume that neither degree of roasting nor method of preparing the infusion need be further considered as appreciably affecting the rather generous limiting values suggested for the first three ratios. It might also justifiably be assumed that none but unusual varieties of coffee will give ratios departing to any appreciable extent from those already suggested, though, to adopt a counsel of perfection, it might be desirable to examine as complete a range of coffees of various origin as it is possible to obtain. This is obviously a task beyond the scope of any but the largest laboratories with access to all kinds of coffee and its adulterants; from our experiments, however, as well as from an examination of published analyses, we are confident that the ratios we have suggested will very seldom, if ever, be found to be wide of the mark.

CALCULATION OF AMOUNT OF ADULTERATION.—It must be stated at once that the determination of the *exact* amount of adulteration in a coffee infusion is probably impossible, owing to a number of factors, such as natural variations, different methods of preparation, and so on. It will be seen, however, that it is possible to obtain a fairly approximate figure by either of the following two alternative methods of calculation.

Method 1.—It has been found that the percentage of ash in the decoction is approximately the same whether this is prepared from pure coffee or from coffee admixed with chicory, and depends only on the concentration of the decoction. For pure coffee the ratio of extractives to ash is about 6 to 1. Again, for pure coffee the ratio of extractives to caffeine is about 20 to 1. Hence a fair approximation to the percentage of coffee in the mixture used for making the decoction may be obtained as follows:

Multiply the percentage of ash by 6 and use this figure as extractives which should be present if the liquor is prepared from 100 per cent. coffee—

$$\text{Ash per cent.} \times 6 = X.$$

Multiply the percentage of caffeine by 20; this gives extractives due to coffee in the liquor—

$$\text{Caffeine per cent.} \times 20 = Y.$$

Then

$$\text{Coffee per cent.} = \frac{Y \times 100}{X}$$

For *genuine* coffee Y will never be lower than X, and hence the percentage of coffee indicated will always exceed 100.

If the amount of adulteration in any given sample indicated by the use of the formula, (caffeine × 20), is small, re-calculate, using the formula, (caffeine × 24). This will give a maximum figure for coffee, thus giving further advantage to the vendor, which is advisable, since it is better to under-estimate the amount of adulteration, and so be able to show in Court that the given figure errs only on the side of leniency.

Method 2.—Let total extractives found = T, and extractives due to coffee in the liquor = Y (Method 1). Then extractives due to *chicory* in the liquor = (T − Y) = Z.

Taking the percentage of extractives in coffee as 24 per cent., and that in chicory as 70 per cent., we get—

$$\text{Percentage w/v of coffee used in preparing the decoction} = \frac{Y \times 100}{24} = A$$

$$\text{and ,, ,, ,, chicory ,, ,, ,, ,, ,,} = \frac{Z \times 100}{70} = B.$$

From A and B the percentages of coffee and chicory in the mixture used for making the decoction are obtained by—

$$\text{Coffee per cent.} = \frac{A \times 100}{A + B} \text{ and chicory per cent.} = \frac{B \times 100}{A + B}$$

In the above calculation (Method 2), it is assumed that the total extractives are removed from coffee and chicory in preparing the infusion. As this assumption will not always hold good, especially if the method of making the infusion is a mild one, it may be found that the percentages of coffee and chicory, as calculated, may not always agree with those obtained by Method 1. As a rule, however, the results agree well—see Table VIII.

We have tested these schemes on several samples of coffee infusions submitted to us, the actual composition of which was not revealed until after we had reported our figures. The results are given fully in Table VIII, and it will be well to let the figures speak for themselves. It may again be emphasised that, although the last two ratios given in this table are very characteristic for this batch of samples, it has been found by later extended work that the figures for chloroform extract are too variable to be relied upon in every instance. They may, however, sometimes prove useful for confirmation. For example, since the ratio of extractives to chloroform extract can never exceed that of extractives to caffeine (limiting value 24 to 1), and the ratio of ash to chloroform extract can never exceed that of ash to caffeine (limiting value 4 to 1), if it be found that these ratios exceed these limiting values, adulteration is confirmed; if, however, they are below the limiting values, no useful deduction can be drawn from them, and the other ratios must be relied on for purposes of calculation.

TABLE VIII

"COFFEE" INFUSIONS

	1	2	3	4	5	6	7
Extractives per cent.	2·30	2·28	2·61	3·50	4·53	5·35	5·75
Ash ,, ,,	0·37	0·358	0·38	0·407	0·401	0·404	0·375
Chloroform extract per cent.	0·172	0·171	0·114	0·088	0·076	0·036	0·029
Caffeine ,, ,,	0·115	0·118	0·095	0·081	0·057	0·040	0·006
Ratios :							
Extractives to caffeine	20·0/1	19·3/1	27·4/1	43·2/1	79·1/1	133·7/1	920·0/1
Extractives to ash ..	6·2/1	6·4/1	6·9/1	8·4/1	11·3/1	13·2/1	15·3/1
Ash to caffeine ..	3·2/1	3·0/1	4·0/1	5·0/1	7·0/1	10·0/1	62·5/1
Extractives to chloroform extract ..	13·4/1	13·3/1	22·9/1	39·8/1	59·6/1	148·6/1	198·3/1
Ash to chloroform extract ..	2·1/1	2·1/1	3·3/1	4·6/1	5·3/1	11·3/1	13·1/1
Percentage coffee as found by analysis—							
By method 1 ..	100	100	83·3	66·5	47·5	33·0	5·3
,, ,, 2 ..	100	100	88·7	71·6	49·5	33·9	5·8
Composition as prepared—							
Coffee per cent. ..	100	100	90·0	75·0	50·0	25·0	10·0

Finally, we have examined seven samples of black coffee obtained from restaurants. Numbers 1 to 4 were taken from tea-shops of four firms having branches all over the country, and the remaining three from small London restaurants. Samples 1 to 5 were found to be genuine coffees, unsweetened, and the actual results obtained are given in Table IX, from which it is apparent that the ratios of extractives to caffeine, extractives to ash, and ash to caffeine, are all within the limits suggested for pure coffee. It may be pointed out that for routine examinations of such samples as these all that is probably necessary is the determination of the ratio of extractives to ash; regard should be paid, however, to the general character of the sample and further determinations carried out if deemed necessary.

TABLE IX

SAMPLES OF "COFFEE" INFUSIONS FROM RESTAURANTS

	1	2	3	4	5
Extractives per cent.	1·356	1·328	1·820	1·480	1·170
Ash ,, ,, ...	0·219	0·224	0·279	0·223	0·189
Caffeine ,, ,, ...	0·078	0·062	0·097	0·080	0·059
Ratios :					
Extractives to caffeine	17·5/1	21·6 /1	18·8 /1	18·5/1	19·7/1
Extractives to ash	6·2/1	5·94/1	6·5 /1	6·6/1	6·2/1
Ash to caffeine	2·8/1	3·6 /1	2·88/1	2·8/1	3·2/1

The sixth sample in this batch was not a genuine coffee infusion, but was probably prepared from sweetened coffee and chicory extract. In addition to the usual constituents, sugars were also determined, in order to arrive at the "true extractives." The following results were obtained:

Total solids	1·37 per cent.
Sugars	0·91 ,, ,,
True extractives (by difference)	0·46 ,, ,,
Ash	0·046 ,, ,,
Caffeine	0·006 ,, ,,
Ratio of extractives to caffeine	76 to 1
Ratio of extractives to ash	10 to 1
Ratio of ash to caffeine	7·6 to 1

The above ratios prove conclusively that the liquid was not prepared from pure coffee; in fact, the first two would be slightly higher, as no allowance has been made for sugars naturally present in coffee and in chicory. The analytical results show that the coffee and chicory extract from which this infusion was prepared was manufactured from approximately equal parts of coffee and chicory; for, using the equation already given (Method 1), we have:

$$X = \text{Ash} \times 6 = 0{\cdot}046 \times 6 = 0{\cdot}276$$

$$Y = \text{Caffeine} \times 20 = 0{\cdot}006 \times 20 = 0{\cdot}12,$$

$$\text{whence coffee} = \frac{0{\cdot}12 \times 100}{0{\cdot}276} = 43{\cdot}5 \text{ per cent.}$$

The probable composition of the sample was

Dry extract of coffee	0·12 per cent.
Dry extract of chicory and sugars	1·25 ,, ,,
Water	98·63 ,, ,,

When these analytical results are compared with those of numbers 1 to 5, it will be seen that all the genuine samples contained at least 1·2 per cent. of dry extract of coffee.

Sample number 7 gave:

Extractives	0·92 per cent.
Ash	0·082 ,, ,,
Caffeine	0·016 ,, ,,
Added sugar	nil
Ratio of extractives to caffeine	57·5 to 1
Ratio of extractives to ash	11·2 to 1
Ratio of ash to caffeine	5·1 to 1

These results clearly indicate that this sample, also, was not genuine coffee, but was probably prepared from a coffee and chicory mixture, the proportion of coffee to chicory therein being not more than 2 to 1.

Confirmatory evidence of the presence of chicory and other adulterants may often be obtained by a microscopical examination of any grounds or sediment in the sample, and it should hardly need emphasis here that the analyst should have regard to the possibility of interfering factors; for instance, if a sample has been prepared from a coffee and chicory extract containing benzoic acid or its derivatives as preservative, he should make due allowance for this in the determination of extractives; similarly, he should make due allowance, wherever necessary, for the presence of any other foreign ingredient.

In conclusion, it would appear reasonable to infer that the three ratios of extractives to caffeine, extractives to ash, and ash to caffeine, will detect with a reasonable degree of certainty adulteration exceeding about 10 to 15 per cent. in coffee infusions. But adulteration below this limit could probably not be certified with any degree of confidence, as allowance must be made for natural variations, and also for variations in the method of preparation, degree of roasting, and so on.

METHODS OF ANALYSIS.—*Extractives.*—Filter the infusion through a fluted filter-paper and evaporate 50 ml. of the filtrate to dryness on the water-bath, and finally in the water-oven, to constant weight.

Ash.—Determine as usual on 100 ml. of the infusion filtered through fine muslin.

Chloroform Extract.—To 100 ml. of the infusion, filtered through fine muslin, add about 10 ml. of ammonia (sp.gr. 0·880), followed by 25 ml. of chloroform, shake vigorously for about 2 minutes and allow to stand overnight. The chloroform layer separates out on gently rotating the separating funnel. Draw off the chloroform into another separator and wash with about 20 ml. of water. Repeat the extraction with chloroform four times, allowing 2 hours for the layers to separate, and washing the extracts successively with the same 20 ml. of water in the second separator.

Recover the chloroform by distillation from the combined extracts, dry the residue and weigh.

Caffeine.—For the accurate determination of caffeine it is necessary to determine the nitrogen-content of the chloroform extract by means of the Kjeldahl process. The factor for conversion of nitrogen into caffeine is 3·464. We made use of the procedure, suggested by Moir and Hinks,[7] of the addition of sucrose, before digestion with sulphuric acid, to ensure the conversion of alkaloidal nitrogen into ammonia without loss.

The following procedure was found to minimise the frothing:

Add 5 ml. of sulphuric acid (nitrogen-free) to the flask containing the dry chloroform extract and warm on the water-bath for about 5 minutes, with gentle shaking. Transfer to a Kjeldahl flask, washing in with a little water. Add 5 ml. more of sulphuric acid and repeat as described above, washing the flask with a little more water. Gently boil to remove the water, and *then* add about 0·2 g. of sucrose and digest till colourless, using copper sulphate or selenium powder as catalyst. Determine the ammonia as usual by distillation into 20 ml. of 0·1 *N* acid.

If the amount of caffeine to be determined is very small—say, of the order of 5 mg.—it is advisable to use direct Nesslerisation of the digestion mixture, as suggested by Moir and Hinks.[7]

Sugars.—These should be determined only if the ratio of extractives to ash exceeds 7 to 1. The coffee infusion may be clarified as usual with neutral lead acetate, and for the determination of reducing sugars in coffee preparations before and after inversion the process which we have found very suitable is the one generally referred to as Bertrand's method.[8,9,10]

The greater part of this investigation was undertaken at the request of the

Coffee Section of the British Empire Producers' Organisation, to whom, and to the Coffee Board of Kenya, we desire to tender our thanks for the supply of coffees of known origin and degree of roasting, as well as for their kind permission to quote results which formed part of our several reports to them while the work was in progress.

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ANALYTICAL LABORATORIES
ROYAL DENTAL HOSPITAL
LEICESTER SQUARE, LONDON, W.C.2

DISCUSSION

Mr. E. HINKS asked the authors if they had considered to what extent these ratios, and the conclusions drawn from them, might be affected by the presence of caramel and other additions differing in ash-content and in other respects from both coffee and chicory.

Mr. E. R. BOLTON recalled the work published many years ago by Tatlock and Thomson which he had found useful at the time, and he would be interested to know how the ratios now worked out compared with the data published by these authors.

Mr. A. W. KNAPP said that in the roasting of coffee it was generally assumed that some caffeine was sublimed, the amount varying with the duration of the roasting and the temperature attained. This varying loss might interfere with the proposed ratios. It was also generally assumed that the theobromine was lost when cacao was roasted, but he could find no evidence of this in practice. However, coffee was roasted at a much higher temperature than cacao and loss of caffeine might reasonably be expected.

Dr. H. E. Cox thought that the ratios so clearly brought out by the authors would be of great value in mixtures known to contain only coffee and chicory; but it seemed possible that small additions of other substances, such as mineral salts or caffeine, would seriously disturb them. Hence, much care would be needed in applying the ratios to unknown products.

Dr. H. R. NANJI, replying, said that the method employed for the determination of caffeine was simply extraction with chloroform from the infusion made alkaline with ammonia, and determination of the nitrogen in the chloroform extract. They found it necessary to add sucrose to the acid digestion mixture, as suggested by Moir and Hinks, because, without this precaution, they obtained slightly low results. The difficulty arising from the presence of added caramel, mentioned by Mr. Hinks, was a real one in certain cases, mainly in coffee extracts and infusions prepared from them. The suggested method of calculation (Method 2), in which the ash was not taken into consideration at all, overcame the complication due to any abnormal ash in the added caramel. He was obliged to Mr. Bolton for his reference to Tatlock and Thomson's earlier paper, and reference would be made to it in the present paper when this was printed.

Replying to Mr. Knapp, he said that some small loss of caffeine during roasting might undoubtedly occur, but there was also loss of moisture, and the net percentage of caffeine remained about the same. In reply to Dr. Cox, he pointed out that they did not propose to rely alone on ratios involving the ash-content. Several other ratios were used, involving extractives, caffeine and so on. In answer to a question by Mr. Stevens as to the adulteration of coffee with substances other than chicory, Dr. Nanji observed that these adulterants showed marked chemical and microscopical differences. Speaking generally, in infusions prepared from coffee so adulterated there would probably be deficiency in caffeine, higher figures for extractives and carbohydrates, and, moreover, the ash and the alkalinity of the ash might be different. Determinations of all these would be helpful. The authors were confident that the three ratios—extractives to caffeine, extractives to ash, and ash to caffeine, taken together, would usually detect adulteration. Again, most of the adulterants of coffee contained starch and therefore a simple test with iodine on a decoction decolorised by acidified permanganate was very useful; the absence of starch ruled out a number of adulterants, such as toasted bread crumbs, acorns, rye, wheat, bean, pea, gram (chick pea), and so on.

Mr. F. W. Edwards, dealing further with the adulterants of coffee other than chicory, remarked that in certifying adulteration it might be found preferable to use some form of words, such as "extractives due to ingredients other than coffee" rather than to specify a particular adulterant, especially as specific tests for some were not known. If any definite evidence of the nature of the adulterant were available, it could always be produced in Court.

An Investigation into the Methods of Toxicological Analysis of Viscera

By C. G. DAUBNEY, M.Sc., A.I.C., and L. C. NICKOLLS, M.Sc., F.I.C.

PART I. THE EXTRACTION OF ALKALOIDS FROM VISCERA

Introduction.—The methods available for the examination of viscera for the presence of alkaloidal poisons are, in general, based on the original work of Stas.[1] Modifications have been introduced by subsequent workers, but the essentials of the process remain the same and are as follows.[2,3]

The material is minced and extracted in dilute acid solution with water or 50 per cent. alcohol, and the extract is filtered and evaporated to low bulk. Separation of the alkaloids from proteins and glycogen in the residue is effected by extraction with absolute alcohol, the alcohol being evaporated between extractions, and separation from fat is effected by extraction with acidulated water, and the alkaloids in the final water extract are then isolated by extraction from alkaline solution with an appropriate solvent. Modifications have been introduced to increase the purity of the final aqueous extract by the use of precipitants such as lead acetate,[4,5] or the use of clarifying agents such as charcoal. Such modifications, however, are very dangerous in practice, as, in general, protein precipitants are also alkaloid precipitants, while substances such as charcoal strongly and retentively adsorb alkaloids. Stas[6] condemned the use of both substances.

Workers in this field encounter a number of difficulties owing to the nature of the material, which renders lengthy and tedious the quantitative extraction of relatively small amounts of alkaloids from tissues. Moreover, many of the quantitative extraction experiments in the literature are of little value, owing to the difficulty of obtaining the requisite conditions, *viz.* the absorption of a known weight of alkaloid in the cells of a quantity of tissue and the subsequent extraction of this alkaloid therefrom.[7]

We are not concerned here with the determination of alkaloids in cases where a large dose of poison has been consumed and, death rapidly following, the bulk of the poison is present in the stomach contents. The quantitative determination of alkaloids by the classical methods in stomach contents and also in urine is quite straightforward. The type of case which is of interest is that in which an approximation to a minimum lethal dose of a poison has been absorbed and some time later death ensues, with the poison that has not been destroyed or eliminated disseminated throughout the body. The poison must be sought in the organs, usually the liver or kidneys, where it is present in small amount, such as 0·5 to 4 mg. per 100 g. of tissue.

The present investigation aims at increasing the accuracy, ease and speed of determining alkaloids in viscera.

EXAMINATION OF THE EXISTING METHODS.—A good account of the existing methods as applied to morphine is given by Balls and Wolff.[8] These methods will now be considered to determine where loss is likely to occur.

(i) *Mincing of tissue.*—Beyond general statements to the effect that the tissue must be finely comminuted there is no definite statement in the literature on this point. In determinations involving the addition of alkaloid salts to the tissue the degree of comminution is of little importance, but, when the alkaloid is present in the contents of the individual cells, every cell must be ruptured to extract its contents, and the degree of comminution is important. With coarse mincing, loss from this cause is inevitable.

(ii) *Extraction of the minced tissue.*—Two points arise under this heading. First, the penetration of all the cells of the tissue and the removal in solution of the alkaloid-content; and secondly, the quantitative separation of the solution from the very bulky cellular detritus. The finer the mincing the better the penetration, but the greater the difficulty of obtaining a satisfactory separation of the alkaloid solution from the finely divided extracted tissue. There is also to be considered the possibility of the adsorption of the alkaloids by the very finely divided protein precipitate.

In some experiments we have found that finely divided precipitated protein does not appreciably adsorb either morphine or quinine from aqueous solution. In the presence of large amounts of strong electrolytes, such as ammonium sulphate and sodium chloride, however, such protein, while still not adsorbing morphine, quantitatively and retentively adsorbs quinine. This may account for some of the conflicting statements in the literature.

(iii) *Alcohol treatment of the residue after evaporation.*—As much as 100 g. of gummy residue may be obtained from the evaporation of the extract from one kg. of tissue. The residue is very sticky and largely insoluble in alcohol, and yet must be extracted by alcohol until free from alkaloids. Various methods are given for granulating this residue to assist extraction, but our experience is that it is difficult to free the mass from alkaloid, and that loss may occur at each stage of the extraction with alcohol.

(iv) *Separation from fat by an aqueous extraction.*—Occlusion of alkaloid in the fat occurs to a certain extent. Unless precautions are adopted, some loss is experienced. This, however, is not one of the serious sources of loss. Attempts to extract the alkaloid from solid or liquid fat with acidulated water did not give 100 per cent. yields. The fat must either (*a*) be dissolved in petroleum spirit and the alkaloid extracted from the petroleum spirit solution with acidulated water, or (*b*) be dissolved in a little petroleum spirit, acidulated water added, the petroleum spirit removed by warming, and the aqueous solution filtered into the separating funnel. We have used the latter of the two alternatives.

(v) *Extraction of the alkaloids with immiscible solvents.*—No loss should occur here. In fact, the difficulty is to prevent a fictitiously high result. The final aqueous extract of the tissue weighs between 2 and 10 g. A small proportion of this material, several centigrams, is always extracted by the solvents employed, more particularly when morphine is extracted, and this vitiates the result altogether if the quantity of alkaloid present is small. This is a well-known phenomenon to which constant reference is made in the literature,[7] but most of the methods of purification described are unsatisfactory from the quantitative point of view.

Experiments were carried out, in which two rats, each weighing 200 g., were injected with a mixture of 352 mg. of quinine (as hydrochloride) and 64 mg. of morphine (as hydrochloride). The animals were killed at the end of 20 minutes, minced whole, and the mass was extracted according to the Stas–Otto process, with the following results:

TABLE I

Expt.	Yield and nature of recovered alkaloid	
1	40 per cent.	Very crude
2	41 ,, ,,	,, ,,
3	56 ,, ,,	,, ,,
4	79 ,, ,,	Less crude
5	98 ,, ,,	Moderately pure

Of these five experiments, No. 1 was conducted according to the classical method without any precautions; then progressive modifications were introduced, including adsorption on fuller's earth or silica gel. Expt. 5 was, in effect, conducted in accordance with our final method, to be described later.

These experiments showed that by the simple classical method the extraction tends to be incomplete and the extracted alkaloids to be contaminated with a comparatively large weight of adventitious material. This agrees with the experience of previous workers, with few exceptions.[9,10,11,12]

IMPROVEMENTS IN TECHNIQUE.—In any attempt to improve the existing methods there are two main problems: (1) to extract the alkaloid completely from the tissue, and (2) to recover it from the extract in as pure a form as possible and determine its amount. In this investigation it was found convenient to reverse the order and to study the later stages first.

The alkaloids used in the experiments described later were limited to quinine and morphine. Quinine was chosen for its ready detection at any stage of the operations by the ultra-violet lamp. The morphine was chosen to check the efficiency and applicability of the method.

DETERMINATION OF QUININE.—Quinine can be quantitatively precipitated as an insoluble citrate from ethereal solution,[13,14] but it was found that purification of the crude quinine by means of ethyl acetate and tartaric acid was more satisfactory. The crude quinine is dissolved in ethyl acetate, and insoluble material is removed by filtration. An excess of a saturated solution of tartaric acid in ethyl acetate is added and, after standing overnight, the quinine tartrate precipitate is filtered off, washed with a little ethyl acetate and dissolved in water, and the quinine is extracted from the aqueous solution (rendered ammoniacal) with chloroform. The product is a straw-coloured, brittle resin-like substance consisting of practically pure quinine. A slight correction must be applied for the solubility of the quinine tartrate in ethyl acetate.

The following table indicates the solubility of a few quinine salts in the presence of excess of the acid:

TABLE II

Acid	Solvent	Solubility (calculated as anhydrous quinine)
Tartaric	Acetone	0·095 g. per 100 ml.
,,	Ethyl acetate	0·014 ,, ,, ,, ,,
Citric	,, ,,	0·015 ,, ,, ,, ,,
Oxalic	,, ,,	0·031 ,, ,, ,, ,,

The low solubility of their poly-acid salts in organic solvents appears to be a general property of alkaloids, and further work is in progress with a view to utilising this property for their purification.

PURIFICATION AND DETERMINATION OF MORPHINE.—The standard method described in the literature for purifying morphine is to dissolve the crude extract in amyl alcohol, extract the filtered solution with dilute acid, and re-extract the morphine from the acid extract. We find that the morphine recovered by this method is still impure, and the method finally adopted is as follows:

The chloroform-alcohol extract is shaken with two small portions of water to remove ammonium salts, and then with three small portions of 5 per cent. caustic soda solution. The united aqueous and alkaline extracts are acidified, rendered ammoniacal, and extracted with chloroform and alcohol.[15] The chloroform extract is evaporated to dryness, the residue is extracted with hot ethyl acetate, and this extract is also evaporated to dryness. The purified morphine is dissolved in 30 per cent. alcohol and determined by Mannich's method.[16]

ISOLATION OF THE ALKALOID FROM THE TISSUE EXTRACT.—In view of the difficulty of extracting alkaloids from the sticky mass of proteins, glycogen, etc., and also on account of the tedious nature of the filtrations and evaporations, it seemed advisable to attempt to extract it directly from the extract of the tissue. Lloyd has already shown that this can be achieved with his reagent—a product of fuller's earth—and Gordin and Kaplan[17] have obtained good results in this way, although doubts have been cast on the method. Further recent work suggested that this line of attack was worth following.

Accordingly, the conditions of the adsorption of alkaloids from tissue extracts by fuller's earth and other adsorbents and their subsequent elution were investigated, and the conditions for quantitative extraction were ascertained.

Such adsorption methods had to be discarded later, however, owing to the fact that adsorbents do not adsorb alkaloids quantitatively from strong ammonium sulphate solutions, the use of which is a necessary part of the extraction of the tissue, to be described subsequently.

MINCING AND EXTRACTION OF TISSUE.—We have found it impossible to achieve satisfactory mincing directly with the ordinary type of machine. The following method gives good results and prevents clogging of the mincer:—Cut a sufficient quantity of the organ into pieces suitable for the machine and freeze hard overnight in the ice section of a refrigerator. Cool the mincer and, using the finest cutter, mince the frozen pieces into a tared casserole. Weigh the minced material. On adding 100 to 200 ml. of water, thoroughly stirring and gently warming, the contents of the casserole set to a thick gruel-like mass quite free from lumps. The freezing serves two purposes: (i) the cells tend to rupture owing to the expansion of the contents; (ii) the material is ground up in the solid state, and this results in a fine state of division.

Filtration of the material at this stage is impossible until the protein has been coagulated. To do this, 50 g. of ammonium sulphate and 2 ml. of glacial acetic acid are added for every 100 g. of minced tissue taken, and the whole is heated on the steam-bath until coagulation occurs. The hot mixture is then filtered on a large Buchner funnel, and a clear, pale yellow filtrate is obtained. The drained granular residue is leached with about 200 ml. of hot acidulated water and again filtered.

The advantage of this technique must be emphasised here. The coagulated mass is granular and allows of very rapid filtration, washing and draining, whilst the filtrate is sufficiently free from protein for the alkaloid to be directly extracted from it in a relatively clean condition. The subsequent treatment of the residual mass depends on whether quinine or morphine is present. It has been found that quinine is not extracted to any appreciable extent from organ material by ammonium sulphate solution, but it can be removed by the use of acidulated water. Morphine, on the other hand, is readily extracted by saturated ammonium sulphate solution.

Accordingly, if quinine is sought, the drained residual tissue after the ammonium sulphate treatment is leached with approximately 1½ to 2 litres of hot water containing 1 per cent. of acetic acid, in small successive portions, these combined washings being kept apart from the original ammonium sulphate filtrate. The aqueous leach is first extracted with ether to remove traces of fat if necessary, rendered ammoniacal and extracted five times with 75-ml. portions of ether. Any tendency to emulsify can be prevented by the addition of alcohol. The preliminary removal of fat with ether saturates the aqueous liquor with this solvent. If no preliminary removal of fat is required, sufficient ether is added to saturate the liquid before the five extractions with 75-ml. portions. The combined ethereal extracts are extracted with four 10-ml. portions of dilute sulphuric acid, and the quinine is recovered from the acid liquor, after being rendered ammoniacal, with chloroform. The chloroform is evaporated to dryness, and the crude quinine thus obtained is purified and determined as described above.

If morphine is present, leaching of the residue is continued with a hot saturated solution of ammonium sulphate containing 1 per cent. of acetic acid until some 1½ to 2 litres of total filtrate have been obtained. This is extracted with a small quantity of petroleum spirit to remove fat, if necessary. The aqueous layer is then rendered ammoniacal, and sufficient alcohol (approximately 100 to 150 ml.) to form a small upper layer is carefully added. The morphine is extracted from this mixture with five 100-ml. portions of a 1:1 mixture of chloroform and alcohol. From the combined extracts the morphine is recovered and determined as described above.

ANIMAL EXPERIMENTS.—We are indebted to Dr. J. C. Thomas, of this laboratory, for suggesting the technique of administering the alkaloids, for performing the injections, and for examining a specimen rat to verify the absorption of the alkaloids in the viscera.

TABLE III

QUININE EXPERIMENTS

66 mg.[*] of alkaloid used for each experiment (except No. 8)

Expt.	Material	Yield of quinine Per Cent.	Remarks
1	Liver, 400 g.	Trace	Mass extracted six times with saturated ammonium sulphate solution.
2	Liver, 400 g.	82	Mass extracted six times with acidulated water. Each extract analysed separately. Final extract virtually free from quinine.
3	Liver, 350 g.	77·5	Mass extracted five times with ammoniacal alcohol. Alcoholic extract evaporated to dryness and residue taken up in acidulated water.
4	Liver, 400 g.	74	Mass extracted continuously with acidulated water using a "streamline" filter. Satisfactory leaching difficult.
5	Liver, 400 g.	87	"Streamline" filter used to remove ammonium sulphate liquor. Subsequent extraction with ammoniacal alcohol and acidulated water carried out on Buchner funnel.
6	Liver, 350 g.	72	Mass extracted according to method described in text. Product very pure, but no solubility factor applied.
7	Liver, 450 g.	86	Extraction as described in text. Recovered quinine very pure.
8	Liver, 300 g.	66.5	Used 6·6 mg. of quinine. Liver somewhat decomposed. 4·4 mg. of quinine recovered after purification. Gave strong thalleioquin reaction.
9	Rat (injected) 200 g. +200 g. of rabbit meat	72	Mass extracted with acidulated water. The quinine recovered by adsorption on fuller's earth (50 per cent. yield) and by subsequent ether extraction (22 per cent. yield).
10	Two injected rats (400 g. total)	90	Mass extracted with ammoniacal alcohol. Quinine not completely pure.
11	Two injected rats (400 g. total)	86	Extraction as described in text. Recovered quinine very pure.

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[*] Standard solution of quinine hydrochloride used containing 66 mg. of quinine base per 3 ml.

The experimental rats were injected intraperitoneally with a given quantity of the alkaloid solution. After 20 to 25 minutes they were killed with ether, skinned and frozen overnight, and the whole animal was minced and treated in the manner already described.

The material used in all experiments involving an addition of alkaloids to organic matter consisted of ox or human liver and kidneys, either fresh or in a state of partial decomposition. The liver, etc., was frozen and minced as described, and the required quantity of alkaloid was added to this as a solution in water. The whole was well mixed and warmed on the steam-bath, with stirring. The experimental procedures described were then followed.

TABLE IV

MORPHINE EXPERIMENTS

50 mg.* alkaloid used for each experiment (unless otherwise stated)

Morphine weighed as dinitrophenyl ether (*vide* Mannich's method)

Expt.	Material		Yield of morphine Per Cent.	Remarks
12	1·5 litre of saturated ammonium sulphate solution	CONTROLS	95	Direct extraction with chloroform-alcohol mixture.
13	1·5 litre of saturated ammonium sulphate solution		84	Extracted with chloroform-alcohol mixture and put through purification process.
14	1·5 litre of ammonium sulphate extract of 400 g. of liver		84	Morphine added to sulphate extract after filtration from mass. Standard procedure then followed.
15	Liver, 350 g.		65	One leach with ammonium sulphate solution (40 per cent. yield). Then ammoniacal acetone extraction (25 per cent. yield). Product dirty.
16	Liver, 300 g.		68	One leach with ammonium sulphate solution (50 per cent. yield). Then acid alcohol extraction (18 per cent. yield).
17	Liver, 350 g.		78	One leach with ammonium sulphate followed by acid water.
18	Liver, 400 g.		84	Ammonium sulphate extraction as described in text.
19	Two injected rats (400 g.)		43	One leach with ammonium sulphate solution (25 per cent. yield) followed by ammoniacal acetone (18 per cent.).
20	Two injected rats (400 g.)		63	Standard method as described in text.
21	Two injected rats (400 g.)		48	Standard method as described in text.
22	Two injected rats (400 g.)		55	Standard method as described in text.
23	Three injected rats (400 g.)		42	Standard method. Morphine found includes that in peritoneum (see Expt. 25).
24	Three injected rats (400 g.)		42	As Expt. 23.
25	Six injected rats (1200 g.)		11	Peritoneal cavity washed out and unabsorbed morphine determined. 150 mg. of morphine injected. 17 mg. of morphine recovered from peritoneal washings.
26	Liver, 300 g. + 6 mg. of morphine		100	"Morphine" gave blue colour with Froehde's reagent, and amorphous precipitate with Mannich's reagent. Strong positive result with general alkaloidal reagents.

* Standard solution of morphine hydrochloride used containing 50 mg. of morphine base per 3 ml.

DISCUSSION OF RESULTS.—The technique employed by most workers for the recovery of alkaloids from organs has followed the original work of Stas in one of its modified forms. We have come to the conclusion that by such methods it is difficult and tedious to obtain a good yield of purified alkaloid when the quantity of alkaloid originally present is small.

A few workers have introduced new ideas, such as adsorption of the alkaloid on fuller's earth[17] and papain digestion of the tissue,[12,18] and they claim good yields from quantitative experiments on injected animals, but all the methods are lengthy and often expensive.

In our experiments, the time factor, as well as the expense, has been reduced to a minimum, and a technique evolved which ensures the disruption of the cells of the tissue and produces an extract containing the alkaloid sought with a relatively small amount of protein and other extractives. Further, the recovered alkaloid is obtained in a fairly high state of purity; this avoids an elaborate purification process and attendant loss.

It must be further pointed out that, with morphine, the crude alkaloid directly recovered is sufficiently pure to give satisfactory colour tests and can be precipitated by Mannich's reagent for quantitative determination. This method fails unless the crude alkaloid contains at least 50 per cent. of morphine.

In reference to the results in the quinine experiments given in Table III several points may be mentioned. It will be seen that, starting with about 350 to 450 g. of minced organ, it is possible to recover about 86 per cent. of the 66 mg. of alkaloid present. This figure represents the yield of pure quinine after it has been through a precipitation process and is not just a "purified extract."

Experiments conducted on injected rats gave similar yields, indicating that not only can the quinine be recovered, after it has been absorbed into the animal system, but also that no appreciable loss due to metabolism occurs in the 20 to 30 minutes between injection and death of the animal.

From the controls of the morphine experiments (Table V), it would appear that, working with 50 mg. of alkaloid in 1·5 litres of solution, a yield of about 84 per cent. is the maximum recoverable, and in those experiments in which 50 mg. of morphine were mixed with some 300 to 400 g. of minced organ, this yield has been attained. Again, this figure represents morphine weighed in the form of the dinitrophenyl ether.

The experiments on injected rats, however, gave consistently lower yields, and one can assume that the discrepancy is due to metabolism of the alkaloid.[19] The range of yields in these animal experiments can be ascribed to the individual variations of the rats.

Expt. No. 25 shows that the greater portion of the injected morphine is absorbed into the animal system.

The failure in Expt. No. 26 to recover a product giving the normal colour and precipitation reactions for morphine must be ascribed to a certain amount of decomposition of this substance by biological and atmospheric oxidation, since the extracted "morphine" gave a blue, instead of a violet colour, with Froehde's reagent, and an amorphous, instead of a crystalline, precipitate with Mannich's reagent.

SUMMARY OF METHOD.—(1) Freeze material. Mince into tared casserole while still frozen.

(2) Add one half the weight of water and warm till homogeneous.

(3) Add 50 g. of ammonium sulphate and 2 ml. of glacial acetic acid for every 100 g. of minced material, and warm until coagulated (approx. 65° C.).

(4) Filter on Buchner funnel and wash residue with water.

(5*a*) If quinine is present, extract the residue with successive portions of acidulated water.

(5*b*) If morphine is present, extract the residue with successive portions of ammonium sulphate solution.

(6) Extract the combined filtrates with the appropriate solvent.

(7*a*) Purify the extracted quinine.

(7*b*) Take an aliquot portion of the recovered morphine solution for precipitation with Mannich's reagent, and carry out qualitative tests on the residue.

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METROPOLITAN POLICE LABORATORY
HENDON, LONDON, N.W.9
August 26th, 1937

An Investigation of the Zinc Oxide Separation as applied to the Determination of Manganese in Special Cast Irons

BY ERNEST C. PIGOTT

AT the outset of this investigation it was found that the practice, recommended by many authorities, of neutralising the initial acid solution with sodium carbonate and, prior to oxidation with bismuthate, precipitating introduced chlorides (frequently present in so-called "pure" sodium carbonate) by means of silver nitrate, causes the results to be erroneous. The following table shows the high values obtained when this procedure is adopted:

TABLE I

Sample	C	Si	P	S	Actual Mn content Per Cent.	Result obtained Per Cent.	Error Per Cent.
1/M6 Std.:	3·04	1·47	0·49	0·114	0·61	0·695	+ 13·8
2/M6 Std.:	3·04	1·47	0·49	0·114	0·61	0·71	+ 16·3
3 Wrought iron			..	..	0·16	0·32	+100
4 Wrought iron			..	..	0·16	0·35	+119

The high results were found to be due to the solvent action of silver nitrate upon sodium bismuthate.

Where an aqueous solution of silver nitrate was mixed with an aqueous suspension of sodium bismuthate there was a precipitation of brownish-black silver bismuthate, which dissolved in dilute nitric acid to form an unstable complex; this complex rapidly oxidises ferrous ammonium sulphate in the cold.

Therefore, in the method subsequently investigated, treatment with silver nitrate was omitted, the introduction of chlorides being avoided by using ammonia in place of sodium carbonate.

THE INVESTIGATED METHOD.—The sample (2·2 g.) is dissolved in 50 ml. of dilute (1 : 5) sulphuric acid. The solution is oxidised with 3 to 5 ml. of nitric acid, diluted with cold water to about 200 ml. and treated with ammonium hydroxide (sp.gr. 0·940), with vigorous shaking, until the stage is reached at which any further addition would produce a permanent precipitate. An excess of aqueous zinc oxide suspension is then added, the volume is made up to 500 ml., and, after thorough mixing, 250 ml. are filtered off, the remainder being discarded. This 250-ml. portion, which represents the factor weight (1·1 g.) of the sample, is treated with 50 ml. of nitric acid (sp.gr. 1·2) and about a gram of sodium bismuthate, left for 2 to 3 minutes, and then filtered through an asbestos pad, 2 per cent. nitric acid being used for washing. The filtrate is titrated with $N/10$ solutions of ferrous ammonium sulphate and potassium permanganate, each ml. of ferrous solution being equivalent to 0·1 per cent. of manganese.

It will be seen from Table II that this method, which is used extensively, is excellent for steels, but most unsatisfactory when applied to cast iron, the low results obtained with the wrought iron indicating that the interference is due to some factor other than high carbon-content.

TABLE II

No.	Sample	Actual Mn content Per Cent.	Result obtained	Error Per Cent.	Remarks
1	Steel: C 0·42	0·55	0·545	− 1·0	Concentrated before oxidising with $NaBiO_3$
2	" "	0·55	0·55	nil	
3	Wrought iron	0·16	0·125	−21·8	
4	" "	0·16	0·125	−21·8	
5	Brit. Chem. Std. "G": C Si P S 2·68 1·30 0·45 0·125 per cent.	0·41	0·37	− 9·5	
6	" " " " "	0·41	0·38	− 7·3	
7	Brit. Chem. Std. "L"	1·00	0·90	−10·0	
8	M6 Std.: C Si P S 3·04 1·47 0·49 0·114 per cent.	0·61	0·57	− 6·6	
9	" " " " " "	0·61	0·54	−11·5	Initial solution concentrated
10	" " " " " "	0·61	0·50	−18·0	Initial solution taken to fumes of SO_3
11	" " " " " "	0·61	0·575	− 5·8	
12	" " " " " "	0·61	0·555	− 9·0	Fractionation of $\frac{150}{300}$ ml.
13	Refined iron C Si P S Cr 3·36 2·12 0·19 0·030 3·18 per cent.	1·04	0·94	− 9·6	Oxidised with NH_4SO_4 to remove carbon
14	" " " " " " "	1·04	0·95	− 8·7	
15	" " " " " " "	1·04	0·93	−10·6	

As it was thought that the interference might be due to phosphorus, various amounts of that element, in the form of diammonium phosphate, were added in a series of analyses of a steel of the composition: C, 0·42; Si, 0·46; Mn, 0·55 per cent.; the results were as follows:

TABLE III

No.	Amount of $(NH_4)_2HPO_4$ added	Manganese found Per Cent.	Error Per Cent.
1	None	0·545	−1·0
2	Equivalent to 0·2 per cent. P	0·52	−5·5
3	" 0·35 per cent. P	0·515	−6·4
4	" 0·50 per cent. P	0·51	−7·2

As these results suggested that the loss of manganese was due to chemi-adsorption as the pyrophosphate, attempts were made to eliminate phosphorus prior to the treatment with zinc oxide. Two processes were tried: (*a*) to precipitate the element as zirconium phosphate from the initial acid solution, and (*b*) to cause co-precipitation with metastannic acid from nitric acid solution.

Method (*a*) proved unsuccessful because an excess of the phosphate radical was necessary for precipitation to take place, and method (*b*) gave only a partial separation; the process was obviously inapplicable to the many special irons not readily soluble in nitric acid.

Finally, a double precipitation with zinc oxide, as described in the revised method (*infra*), was found to prevent adsorption losses, giving the following very satisfactory results when applied to different types of cast irons, to some of which chromium sulphate was added in amounts representing up to 10 per cent. of chromium.

TABLE IV

No. of estimation	Cast-iron sample	Amount of $Cr_2(SO_4)_3$ added	Actual Mn content Per Cent.	Manganese found Per Cent.
1	Brit. Chem. Std. "G": C Si P S 2·68 1·30 0·45 0·125 per cent.	nil	0·41	0·41
2	„ „ „ „ „	Equivalent to 1 per cent. Cr	0·41	0·41
3	„ „ „ „ „	Equivalent to 3 per cent. Cr	0·41	0·415
4	„ „ „ „ „	Equivalent to 5 per cent. Cr	0·41	0·405
5	„ „ „ „ „	Equivalent to 10 per cent. Cr	0·41	0·41
6	Brit. Chem. Std. "L"	nil	1·00	0·99
7	M6 Std.: C Si P S 3·04 1·47 0·49 0·114 per cent.	nil	0·61	0·61
8	„ „ „ „ „ „	Equivalent to 3 per cent. Cr	0·61	0·605
9	C Si P S Cr Refined iron 3·36 2·12 0·19 0·030 3·18 per cent.	nil	1·04	1·03
10	„ „ „ „ „ „ „	nil	1·04	1·03

The following revised method, in which is incorporated the double precipitation, may be used with confidence, not only for ordinary cast irons, but also for special cast irons containing chromium, nickel, molybdenum, titanium, copper, aluminium, zirconium, boron, cerium and uranium. In the presence of vanadium it is necessary to make the slight modification of treating the solution with hydrogen peroxide prior to the precipitation of the Group III metals with zinc oxide. If the iron contains cobalt, it is necessary, before the treatment with sodium bismuthate, to precipitate the manganese from the combined filtrates as manganic hydroxide and to dissolve the precipitate, after filtration, in sulphurous acid, adding an excess of nitric acid, and then boiling off the sulphur dioxide.

REVISED METHOD.—The sample (2·2 g.) is dissolved in 50 ml. of dilute (1 : 5) sulphuric acid, the solution is oxidised with 3 to 5 ml. of nitric acid, and, after slight dilution, any graphite is filtered off. Ammonium hydroxide (sp.gr. 0·940) is added until the stage is reached at which any further addition would produce a permanent precipitate, about 30 ml. being required. An excess of aqueous zinc oxide suspension is then added; 7 g. of the oxide is usually sufficient.

After dilution to about 400 ml. the mixture is filtered through a Whatman No. 1 paper, the residue is left unwashed, and half the filtrate is reserved.

The residue is dissolved by passing and re-passing through the filter 80 ml. of hot dilute (1 : 3) sulphuric acid, and finally the paper is washed with hot water. The solution thus obtained is treated with ammonium hydroxide (sp.gr. 0·940) and zinc oxide suspension as before, the volume is made up to 304 ml., and 150 ml. are filtered off. To this is added the reserved half portion of the previous filtrate, 50 ml. of nitric acid are added, and the solution is concentrated to about 150 ml. When cool the solution is treated with about 1 g. of sodium bismuthate, shaken vigorously, left for 3 minutes, and filtered through an asbestos pad, and the residue is washed with 2 per cent. nitric acid. The filtrate is titrated with $N/10$ solutions of ferrous ammonium sulphate and potassium permanganate, each ml. of ferrous solution representing 0·1 per cent. of manganese.

230 Ladykirk Road
Newcastle-upon-Tyne

Official Appointment

Dr. A. G. Francis has been appointed Deputy Government Chemist (November, 1937).

Analytical Methods Committee

SUB-COMMITTEE ON METHODS OF SOAP ANALYSIS

THE DETERMINATION OF UNSAPONIFIABLE MATTER IN OILS AND FATS

The following Note has been authorised for publication by the Council:

Since the publication of the Report of the Sub-Committee appointed to investigate this matter (Analyst, 1933, 58, 203) certain criticisms of the recommended method have been made, on which the Sub-Committee feels that it is necessary to comment.

H. P. Kaufmann (*Fette und Seifen*, 1936, 218) states that in certain cases the amount of caustic alkali specified is insufficient to produce complete saponification of the fat. Examples are given of coconut oil of high saponification value or containing a high percentage of free fatty acids, in which saponification was incomplete. It is important to note that the method specifies alcoholic potassium hydroxide solution *not less than* 0·50 N; if this condition be observed, there is sufficient alkali for extreme cases, even when the *maximum* weight of 2·5 g. of oil is taken.

Criticisms have also been received that the amount of oil taken is insufficient. In the view of the Sub-Committee the quantity of oil is sufficient for all ordinary purposes, but if for any reason it is desirable to obtain a greater weight of unsaponifiable matter than is recovered by the method, the quantity of oil may be increased, provided that the volumes of reagents and solvent are increased in the same proportion. This is essential to the successful working of the method.

It has been stated that methods using petroleum spirit in place of ethyl ether are more convenient for ordinary oils. It was shown in the Report that, while the differences in the results were small for many oils, yet there were many notable exceptions, particularly the fish oils. It was the object of the Report to provide a method which would be generally applicable to *all oils*, and for this reason ethyl ether was chosen.

(*Signed*) H. E. Cox (*Chairman*)
NORMAN EVERS (*Hon. Secretary*)

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

ANNUAL REPORT OF THE CITY ANALYST FOR 1936

OF the 5472 samples examined under the Sale of Food and Drugs Act, 5332 were purchased informally.

COFFEE CONTAINING ROASTED FIG.—A sample labelled "Viennese Coffee" was stated to contain a proportion of "coffee seasoning" described by a trade name and to the identity of which no clue was given. The "seasoning" was found to consist of about 7 per cent. of roasted fig. Exception was taken to the label as not being sufficiently explicit, and the article was withdrawn from sale. A second sample, taken from a fresh consignment, was stated to contain an addition of a fruit seasoning. This, it was considered, gave a more easily understood idea of the contents of the tin. This sample contained about 10 per cent. of roasted fig.

MILK JELLY.—A sample was described on the label as "Milk Jelly," whilst another part of the label bore the words "Contains no milk." There was, therefore, a contradiction in terms, but in view of the fact that the disclaimer as to milk was quite legibly printed on the packet, no administrative action was taken.

VINEGAR AND ARTIFICIAL VINEGAR.—Seventeen of 71 samples were reported as incorrect, the chief offence being the sale of artificial vinegar as genuine vinegar. In most of the cases of substitution an inspector visited the shop and explained the difference between the two articles. No attempt had been made to sell artificial vinegar as malt vinegar. In many instances the cask containing the artificial product was labelled "Pure Vinegar."

One sample was labelled "Pure non-brewed Table Vinegar. Described as non-brewed to distinguish it from malt vinegar." It consisted of artificial vinegar. The term "Table Vinegar" is generally understood to indicate a superior brewed article, and the description on the label was therefore a contradiction in terms. The makers were interviewed, but as no agreement could be arrived at for the proper labelling of the product, its sale was discontinued, and the firm decided to manufacture malt vinegar only.

Essence of Peppermint.—Two of 9 samples were incorrectly compounded. They contained the amount of oil of peppermint specified by the B.P. (10 per cent.), but isopropyl alcohol had been used as the solvent in place of ethyl alcohol. There can be no objection to the sale of the cheaper article as a flavouring material if it is made perfectly clear to the purchaser that it is not "Essence of Peppermint," which is a B.P. designation. Another sample was also made up with isopropyl alcohol and, in addition, contained 12 per cent. instead of 10 per cent. of oil of peppermint. In each instance it was explained by the vendor that the use of the slip label stating the non-official character of the essence had been inadvertently omitted.

H. H. Bagnall

Analytical Methods Committee

REPORTS OF THE SUB-COMMITTEE ON METHODS OF SOAP ANALYSIS

REPORT No. 4

THE DETERMINATION OF FREE ALKALI AND SILICA IN SILICATED SOAPS

Sub-Committee

Nominated by the Government Chemist.—F. R. Ennos, B.A., B.Sc., F.I.C.
Nominated by the London Chamber of Commerce and Messrs. Unilever, Ltd.—B. D. W. Luff, F.I.C.
Nominated by the London Oil and Tallow Trades Association.—E. R. Bolton, M.I.Chem.E., F.I.C.
Nominated by the Society of Public Analysts and Other Analytical Chemists.—H. E. Cox, D.Sc., Ph.D., F.I.C. (Chairman), D. E. Davis, B.Sc., F.I.C., W. H. Simmons, B.Sc., F.I.C., and N. Evers, B.Sc., F.I.C. (Hon. Sec.).

In the third Report of the Sub-Committee published in The Analyst (1937, 62, pp. 36–41), on "The Determination of Free Alkali in Soaps," it was stated that the methods there recommended could not be applied without modification to silicated soaps.

The present Report contains recommendations of special methods for silicated soaps based on further work carried out by members of the Sub-Committee.

Preliminary tests showed (*a*) that the determination of total free alkali, as recommended in Report No. 3, by the addition of excess of sulphuric acid and titration of the excess of acid with phenolphthalein as indicator, is not satisfactory for silicated soaps, and (*b*) that the determination of free hydroxide alkali by the addition of barium chloride is also inapplicable to these soaps.

Free Caustic (Hydroxide) Alkali.—The commonly used method of extraction of the soap with hot alcohol and titration of the solution to phenolphthalein was tried with silicated soaps, but it appeared that caustic alkali is continuously extracted by hot alcohol from the residue remaining after the soap has been removed, when alkaline silicate is present in the residue. It has not therefore been found possible to distinguish between free caustic alkali from the soap and that from alkaline silicate. The following method is recommended as giving an empirical value which provides a useful indication of the apparent caustic alkali present:

Boil 100 ml. of industrial alcohol (66° o.p.; 96 per cent. by vol.) to remove carbon dioxide. Add 0·5 ml. of a 0·5 per cent. solution of phenolphthalein and neutralise at 70° C. with 0·1 *N* acid or alkali. Add 10 g. of the soap in thin shavings and heat on a water-bath, breaking up the insoluble residue with a glass rod, if necessary, in order to effect complete solution of the soap. Allow to settle and decant 50 ml. of the clear liquid. Titrate at 70° C. with 0·1 *N* sulphuric acid until the pink colour just disappears. Calculate the apparent free caustic alkali as Na_2O (1).

THE DETERMINATION OF FREE ALKALI DUE TO CARBONATE AND SILICATE.—The insoluble residue from the above determination of apparent free caustic alkali includes carbonate and silicate together with any other filler. Qualitative tests should be made to ascertain the absence of borax, phosphate, or other interfering substance (zinc oxide does not interfere). If these are absent, the following method, which has been found satisfactory, is recommended. Filter the insoluble residue from the determination of free caustic alkali and wash the residue with 20 ml. of hot alcohol previously neutralised at 70° C. Dissolve the residue in about 50 ml. of water, pour through the filter, and wash the insoluble residue with water. Titrate the solution and washings with 0·5 *N* sulphuric acid, using methyl orange as indicator. Calculate the result as Na_2O (2).

Next determine the carbon dioxide on another portion of the soap or on the residue insoluble in alcohol by expelling the carbon dioxide by means of dilute sulphuric acid and absorbing the evolved gas in potassium hydroxide solution in the usual way. The apparatus used should be one which includes a condenser in its train, as it is necessary to heat the acidified soap solution in order to ensure complete evolution of the carbon dioxide. From the weight of carbon dioxide the equivalent Na_2O as carbonate is calculated (3). The difference between (2) and (3) gives the Na_2O due to silicate.

Various methods for the determination of combined alkali have been investigated, but these methods did not afford satisfactory results on account of the indefiniteness of the end-points. The Sub-Committee, however, recommends the following procedure for the determination of the *total free and combined alkali*. This method affords a useful check on the accuracy of the separate determinations.

Dissolve about 5 g. of the soap in hot water, rinse into a separator, and add a slight excess of 0·5 *N* sulphuric acid. Extract the fatty acids with three quantities of ether and wash the combined ethereal solution three times with water. After evaporating the ether from the combined aqueous liquids titrate the excess of acid with 0·5 *N* alkali, using methyl orange as indicator. The acid used corresponds to the sum of total free alkali (caustic, carbonate, and silicate) and alkali combined as soap. Evaporate the ether from the combined ethereal solutions and dry and weigh the fatty matter. Determine the neutralisation value by dissolving a weighed portion in alcohol and titrating with 0·5 *N* alcoholic potassium hydroxide solution. From this value calculate as Na_2O the alkali combined as soap. The difference between the total free and combined alkali and alkali combined as soap should be found to agree with the sum of the three separate determinations of free caustic, carbonate, and silicate alkali.

THE DETERMINATION OF SILICA PRESENT AS ALKALINE SILICATES.—The standard method of the American Chemical Society (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 5) has been investigated, among others, by the Sub-Committee, and is recommended. The following is a description of the method.

(*a*, 1) When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not more than 0·2 g. of silica in a platinum dish at a low temperature. After charring, extract the soluble salts with water, return the paper and charred residue to the dish, and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 ml. of strong hydrochloric acid in excess. The dish or casserole containing the solution should be covered with a watch glass during the addition of acid so as to avoid loss by spray.

(*a*, 2) When the material contains mineral matter insoluble in water take a portion, containing not more than 0·2 g. of silica, of the solution obtained by titrating the free alkali due to carbonate and silicate, as described on p. 868, and add 5 to 10 ml. of strong hydrochloric acid.

(*b*) Evaporate the acidified solution (washing off and removing the cover-glass if used) to dryness on a steam-bath or hot plate at a temperature not exceeding 200° C., with care to avoid loss by spirting. Cool, moisten with concentrated hydrochloric acid, and let stand 5 to 10 minutes, breaking up all lumps with a stirring rod. Add about 25 ml. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering through a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, then over the blast lamp. Cool in a desiccator, weigh, and repeat until constant weight is obtained. Moisten the contents of the crucible with water, add 10 ml. of hydrofluoric acid and four drops of strong sulphuric acid, evaporate to dryness over a low flame, ignite at the temperature of the blow pipe for about 2 minutes, cool in a desiccator, and weigh. The difference between this weight and the previous weight is the weight of the silica (SiO_2).

The results obtained by members of the Sub-Committee on two samples of silicated soap are shown in the table.

SOAP A

ALKALI CALCULATED AS Na_2O PER CENT.

	Observer				
	A	B	C	D	E
Apparent free caustic alkali (1)	0·04	0·03 0·02	0·011	0·01	0·01 0·01
Alkali due to carbonate and silicate (2)	4·13	4·12 4·12	4·12	4·22	4·15 4·17
Total free alkali (1 and 2) ..	4·17	4·14 4·14	4·13	4·23	4·16 4·18
Carbonate alkali (3)	0·03	—	0·08	—	0·03 0·04
Total free and combined alkali ..	8·96	8·95 8·92	8·86 8·93	9·02 8·98	8·95 8·96
Total fatty matter	38·29	38·42	38·68	37·9	38·15 38·14
Mean mol. wt.	251	254·5	254	255	257
Alkali combined as soap (calculated from above)	4·69	4·67	4·71	4·61	4·59
Total free alkali (by difference)	4·27	4·27	4·19	4·39	4·36
Silica (as SiO_2)	11·21	11·23	11·32	11·25	11·03 11·08

Soap B

	Observer				
	A	B	C	D	E
Apparent free caustic alkali (1)	0·15	0·16 0·12	0·12 0·18	0·15	0·13 0·14
Alkali due to carbonate and silicate (2)	3·81	3·72 3·78	3·76	3·65 3·68	3·70 3·68
Total free alkali (1 and 2) ..	4·08	3·88 3·90	3·92	3·82	3·83 3·82
Carbonate alkali (3)	0·10	0·30	0·10	0·14	0·13
Total free and combined alkali..	9·39	9·14 9·18	9·10 9·19	9·20 9·18	9·19 9·16
Total fatty matter	41·53	40·58	42·92	41·2	40·64 40·64
Mean mol. wt.	243	244·5	245	245	247
Alkali combined as soap (calculated from above) ..	5·31	5·14	5·42	5·21	5·10 5·10
Total free alkali (by difference)	4·08	4·02	3·73	3·98	4·03
Silica (as SiO_2)	7·31	7·38	7·10	7·14	6·83 6·84

(*Signed*) H. E. COX (*Chairman*)
NORMAN EVERS (*Hon. Secretary*)

REPORT No. 5

THE DETERMINATION OF ROSIN IN SOAPS

In continuation of its work on the investigation and standardising of methods for the analysis of commercial soaps, the Sub-Committee has examined methods for the determination of rosin. In addition to its meetings and the discussion of results obtained experimentally by its members, the Sub-Committee has had the advantage of drawing on the experience of certain soap makers who have themselves investigated this problem and its labours have been thereby shortened.

There are two methods commonly used for the determination of rosin in soap both of which depend upon the fact that when a mixture of resin and fatty acids is heated with an alcohol in presence of a suitable agent the fatty acids are esterified, whereas the resin acids remain unchanged. The two methods are (*a*) the Twitchell method (*J. Soc. Chem. Ind.*, 1891, 804), as modified by Wolff and Scholze (*Chem.-Ztg.*, 1914, **38**, 369, 382, 430), in which esterification of the fatty acids is effected by means of sulphuric acid and ethyl alcohol, and (*b*) the McNicoll method (*J. Soc. Chem. Ind.*, 1921, **40**, 124T), using naphthalene-2-sulphonic acid and methyl alcohol as the esterifying agents.

Wolff's method is still adopted in modified form as the official method by the Committee on Analysis of Soaps and Soap Products of the American Chemical Society (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 1), but, in our opinion, it is long and troublesome. In this method the result is calculated as rosin, the mean molecular weight being taken as 346, whereas in the McNicoll method, as adopted in the Government Department Specifications for General Stores, No. T.G. 23 (Soaps, 1929), it is recommended that the result be calculated as resin acids using the factor 326. The Sub-Committee prefers this method of expression as the more accurate, since it does not include the unsaponifiable matter of rosin, which is a varying quantity. McNicoll's method and Wolff's modified method, as described by the U.S. Committee (*loc. cit.*), have been carried out on a sample of soap by members of the Sub-Committee, and the results are set out in Table I.

TABLE I

RESIN ACIDS AS PERCENTAGE OF TOTAL FATTY MATTER

Observer	McNicoll's method (factor 326)	Wolff's method (factor 326)
A	10·6	
	10·5	10·9
	10·6	
B	11·1	11·2
	11·3	11·3
C	—	11·3
D	11·0	11·5
	10·9	11·4
E	10·9	10·9

Because of the closeness of these results and the greater speed and convenience of the McNicoll method the Sub-Committee recommends its adoption.

McNicoll does not suggest any correction of the results, though he indicates that certain small errors are inherent in these esterification processes. The Government Stores Publication advises a deduction of 2 per cent. independent of the percentage of resin acids present. The U.S. Committee states that Wolff's method gives somewhat high results with low-rosin and approximately correct results with high-rosin soaps. Table II shows the approximate excess of resin acids to be expected by the McNicoll method.

TABLE II

MCNICOLL METHOD

Tallow fatty acids and rosin mixture. Rosin, per cent.	Actual resin acids in mixture Per Cent.	Resin acids found (Mol. wt. of resin acids, 326) Per Cent.
0	0	1·6
10	9·2	10·0
15	13·8	15·0
20	18·4	19·7
30	27·6	28·8
100	92·0	91·8

These results are typical of a larger number of experiments which have been carried out in the laboratories of members of the Sub-Committee.

The Sub-Committee therefore recommends that a deduction of 1 per cent. be made from the results obtained by McNicoll's method independent of the percentage of resin acids found, and the following procedure is advised:

Reagents.—(1) A solution of naphthalene-2-sulphonic acid (40 g.) in pure dry methyl alcohol (1 litre); (2) $N/5$ alcoholic potassium hydroxide solution.

Method.—Separate the total fatty matter from about 5 g. of the soap by dissolving in hot water, acidifying with dilute sulphuric acid, cooling and washing the cake of fatty matter with water until the aqueous washings are free from acidity. The fatty matter may also be obtained by extraction with ether from acid solution as in the determination of total alkali (Report No. 4). Weigh about 2 g. of the total fatty matter into a 150-ml. flask, dissolve it in 20 ml. of the naphthalene-2-sulphonic acid reagent and boil gently under a reflux condenser for 30 minutes, adding small pieces of pot to ensure regular ebullition. Carry out a blank test at the same time with 20 ml. of the reagent alone. Cool the contents of both flasks and titrate with $N/5$ alcoholic potassium hydroxide, using 0·5 ml. of 0·5 per cent. alcoholic solution of phenolphthalein as indicator. The difference between the two titrations is a measure of the resin acids. One ml. of $N/5$ alcoholic potassium hydroxide is equivalent to 0·0652 g. of resin acids. Calculate the resin acids as a percentage of the total fatty matter and subtract 1 per cent. from the percentage so obtained.

When the percentage of rosin is small (less than 5 per cent.) it is not expected that the results will be so accurate as with larger rosin contents. It is presumed that in all such cases the presence of rosin has been established qualitatively by the Liebermann-Storch test. The quantitative method is liable to give erroneous results with certain types of carbolic soaps containing high-boiling tar acids.

For the purpose of calculating the approximate proportion of rosin in the soap it may be assumed that rosin contains 92 per cent. of resin acids.

(*Signed*) H. E. Cox (*Chairman*)
Norman Evers (*Hon. Secretary*)

Ministry of Health

SALE OF FOOD AND DRUGS

Extracts from the Annual Report for 1936–1937 and Extracts from the Reports of Public Analysts for the Year 1936

Appointment of Analysts.—During the year 1936 approval was given to the appointment of 29 Public Analysts.

Adulteration.—The total number of samples of food and drugs analysed by Public Analysts in England and Wales during 1936 was 146,438; this is the highest number recorded. Of these samples, 7802 were reported against (5·3 per cent. as against 5·5 per cent. in 1935).

Preservatives.—Of the 415 samples, 203 contravened the Regulations relating to sausages, usually for containing sulphur dioxide in amounts that would have been permissible if declared. Boron preservative was found in several articles, including sausages, butter, wafer biscuit, and potted and other meats. Formaldehyde was reported in several samples, including milk and cheese, and sodium fluoride was found in samples of wine. Samples of meat paste and canned fish contained benzoic acid. Two samples of grape fruit squash contained salicylic acid in addition to a small proportion of sulphur dioxide. Articles containing sulphur dioxide contrary to the Regulations included meat and meat products, mustard and vinegar. A fine of £10 with 10s. costs was imposed in one case for the sale of chitterlings containing a boron preservative.

Milk.—Of the 80,082 samples examined, 5706 were reported to be adulterated or not up to standard. There were 1255 "appeal to cow" samples, of which 460 were found to be below the presumptive standard of the Sale of Milk Regulations, 1901. Nine samples contained dirt and 6 contained formaldehyde. Two were reported to contain 2·3 and 1·3 per cent., respectively, of cane sugar.

Twenty-six samples of skimmed milk were reported against, mainly on account of added water. One sample was coloured with annatto and one was whole milk.

CONDENSED AND DRIED MILK.—Of 1173 samples of condensed milk examined, 25 were reported against. One contained dirt, one was decomposed, and one contained 160 p.p.m. of tin. Three of the 207 samples of dried milk examined were incorrectly labelled.

CREAM.—Adverse reports were made on 50 of 1852 samples examined, mainly for deficiency in milk-fat. In one case the vendors of a sample of tinned cream which contained 20 per cent. of milk-fat, but was labelled "high concentrated and rich cream," were prosecuted and fined £10 and £3 3s. costs. Another unsatisfactory sample was a synthetic preparation in which less than 15 per cent. of the fat was derived from cream.

BUTTER AND MARGARINE.—Of 7585 samples of butter, 122, and of 2389 samples of margarine, 50 were reported against, mainly for excess of water. Six samples of butter contained boron preservative.

LARD AND OTHER FATS.—Adverse reports were made on 31 of 2674 samples of lard, 2 containing excess of water and the remainder substitute fats. Sixty of the 597 samples of suet were reported against, mainly for containing undeclared or excessive amounts of rice flour or other starchy material. Seven of the 659 samples of dripping were unsatisfactory, 4 containing excess of water and 3 excess of free fatty acids.

CHEESE.—Of the 1465 samples examined, 37 were reported against, mainly for low fat-content. One "cream" cheese contained only 0·5 per cent. of fat. Ten samples contained formaldehyde.

BREAD AND FLOUR.—One sample of bread (containing a large fragment of glass) of the 249 samples examined was condemned, and 3 of the 1285 samples of flour were unsatisfactory.

JAM AND MARMALADE.—Unfavourable reports were made on 128 of the 1620 samples examined. Forty-seven contained excess of preservative and two contained fragments of glass. Other unsatisfactory samples were deficient in fruit or total solids.

VINEGAR.—Of 1787 samples, 173 were reported against; 110 were deficient in acetic acid and most of the other adverse reports were due to the sale of artificial vinegar as "Malt" or "Table" vinegar.

SPIRITS AND BEER.—Of 1553 samples, 46 of whisky, 18 of rum, 17 of gin, and 5 of brandy were below the correct strength. One sample of brandy contained 50 per cent. of spirit other than genuine brandy. Eleven of 489 samples of beer contained excessive preservative, 15 were contaminated with lead, and one with lead and copper.

MISCELLANEOUS ARTICLES OF FOOD.—Over 34,000 samples of other foods of varied description were examined. Thirty-six samples of rice and 4 of barley contained talc or other mineral "facing." "Facing" matter was also found in a number of samples of split peas. Ten samples of pepper contained magnesia or magnesium carbonate, and two samples of black pepper contained pimento. Samples of various spices and of mint contained sand and siliceous matter, and a few samples of mint and one of dried mint contained ailanthus leaves. Excessive quantities of sulphur dioxide were found in 5 samples of sugar, and 17 samples contained tin.

Five samples, sold as coffee, contained chicory, two to the extent of 90 per cent. One sample contained 7 per cent. of roasted fig, and another contained numerous small weed seeds. Three adverse reports were made on "digestive" tea, the labels of which made unjustified statements as to the tannin-content.

Objection was taken to the use of the term "chocolate" in certain articles of confectionery sold as "White Chocolate" or "White Milk Chocolate," but containing no cocoa. Two samples of marzipan were composed of ground coconut and contained no almonds. Some samples of "Cream" cakes and pastries were filled, wholly or in part, with fat other than milk-fat.

Samples of potted meat contained starchy matter or excessive amounts of water. Three adverse reports on fish related to the sale of cat-fish as hake, and two to the sale of witch as fresh sole and lemon sole. One sample of mussels contained benzoic acid, and two samples of canned smoked salmon contained hydroxybenzoic acid and formaldehyde. A sample of bloater paste was found to contain over 80 per cent. of water.

Contamination with tin was reported in 102 samples of canned fish, mainly sild, and 29 samples, mainly of sardines, were contaminated with lead. Tin and zinc were found in two samples of sardine paste. Copper was reported in 3 samples of cider, 2 of glacé cherries, 1 of tomato soup, and 1 of ice-cream. A number of samples of gelatin and of apples and pears were contaminated with arsenic.

DRUGS.—Of the 6431 samples examined, 264 were adulterated. Fifteen samples of sweet spirit of nitre were deficient in ethyl nitrite; 6 of ammoniated tincture of quinine were deficient in ammonia and one contained excess of quinine sulphate. Incorrect proportions of iodine, or potassium iodide, or both, were reported in solutions of iodine. In one sample of iodine ointment no iodine was present, and there was a deficiency of 90 per cent. of potassium iodide.

Thirteen samples of camphorated oil were deficient in camphor, and one contained an excess of that substance. Two samples of cod-liver oil were reported against owing to failure to comply with the British Pharmacopoeia Antimony Trichloride test for vitamin *A*, and another sample was stated to be deficient in vitamin *A* and to have a high acidity. A sample of cod-liver oil emulsion was found to be deficient in cod-liver oil. Carelessness in labelling was apparently the cause of the supply, in one instance, of medicinal paraffin as castor oil, and in another instance of compound glycerin of thymol instead of Parrish's Chemical Food.

Weights and Measures

REPORT BY THE BOARD OF TRADE FOR 1936*

THIS is the Statutory Report to Parliament of the Board of Trade on their proceedings and business under the Weights and Measures Act. The Report also deals with the work of the Standards Department of the Board of Trade under the Sale of Gas Acts, the Coinage Act, 1870, and the Petroleum (Consolidation) Act, 1928.

CUSTODY AND MAINTENANCE OF IMPERIAL AND METRIC STANDARDS.—*Imperial Standard Yard.*—On the occasion of the annual inspection of standards by the Controller a small spot was noticed upon one of the gold studs upon which are engraved the lines by which the standard length is defined. Measurement, then and subsequently, showed that the spot is not extending. It is not possible to take any drastic steps for its removal without endangering the defining lines.

NEW STANDARDS.—A second set of Decimal Avoirdupois weights has been purchased. The subdivided glass measure of 8 fl. oz. is a model of a standard suitable for the use of inspectors in testing quantities of ⅓ pint, a quantity now of importance in connection with the supply of milk to schools.

VERIFICATION OF LOCAL AND WORKING STANDARDS.—The statutory period within which an inspector's local standard weights and weighing instruments are required to be re-verified is five years; for local standard measures the period of legality is ten years. Statements of the verification and re-verification of standards and weighing instruments, and of the standard equipment maintained by local authorities, under the Sale of Gas Acts, for the purpose of testing meters, are given in an Appendix to the Report.

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* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 6d. net.

Examination of Patterns of Weighing and Measuring Apparatus.—*Delivery of Lubricating Oil.*—The accurate delivery of measured quantities of lubricating oil has always presented difficulties, and although patterns have been submitted from time to time, there has invariably been some overriding objection to certification. A certificate (No. 756) has been granted to a pattern incorporating a glass "dispenser." This consists of a glass container fitted with a spring-loaded piston. When this instrument has been clipped into position beneath the nozzle, oil under pressure is forced past a non-return valve and depresses the piston. On lifting a knob which opens the non-return valve the oil may then be expelled by the piston.

Egg-grading Machine.—In a pattern of egg-grading machine approved, a system of electric contacts operated by the movement of the beam is used to illuminate various coloured lights and thus indicate the grade of eggs tested, in accordance with the National Mark Egg Grading Scheme.

Gas Meter showing Therms.—The South Metropolitan Gas Act, 1936, gave power to the company to ascertain therms consumed by gearing incorporated in the meter, and a gas meter fitted with an index designed to do this has been approved. The index is clearly marked to show the purported calorific value of the gas supplied.

Sale of Milk in Cartons.—The Chief Inspector of Weights and Measures, New Zealand, was informed that, in the experience of the Department, the use of cartons as containers for the retail sale of milk in this country has not been found to be detrimental to the purchaser. It was pointed out that milk is required to be sold by certain prescribed quantities under the Sale of Food (Weights and Measures) Act, 1926.

Sale of Seidlitz Powders.—An enquiry has been received from a local authority as to whether an automatic weighing instrument used for the preparation of Seidlitz powders is "use for trade" within the meaning of the Weights and Measures Acts.

The packets are inscribed "Prepared according to the British Pharmacopoeia," and as that publication specifies the quantities of the constituents by weight, it would appear that the inscription on the packet is, in effect, a guarantee implying a contract to supply the constituents in those weights; the element of weight enters into the transaction, and the instrument used to determine that weight may therefore be regarded as subject to the Acts.

Micrometer Caliper Gauges.—In order that inspectors of weights and measures may be in a position to verify the thicknesses of metals when requested to do so, the Department expressed their willingness to test micrometer caliper gauges for the use of inspectors.

The Metric Carat.—The Department has furnished the Keeper of Minerals, British Museum, with a memorandum giving the history and events which led to the legalisation of the metric carat in the United Kingdom by Order in Council in 1913.

International Union of Chemistry

SECOND REPORT OF THE COMMITTEE ON ATOMS

THIS Committee is composed of Dr. F. W. Aston (Chairman), and Professors N. Bohr, O. Hahn, W. D. Harkins, and G. Urbain.

Since the issue of the first Table of Isotopes results have been published enabling revision to be made in the constitution of the following elements:

HYDROGEN.—The isotope of mass 3 is omitted. There is new mass-spectrum evidence that it is not present to the extent of 1 part in 10^{10} in naturally occurring hydrogen.

BERYLLIUM.—The isotope of mass 8 is omitted; it has been shown that it is not present to the amount of 1 in 10,000.

ARGON.—More accurate figures for the abundances of the three isotopes are given.

COBALT.—A second isotope 57 has been discovered and its abundance estimated.

NICKEL.—The presence of isotope 61 has been confirmed.

GALLIUM, BROMINE, RUBIDIUM.—Figures of abundance of the isotopes of these elements have been revised.

STRONTIUM.—A new isotope 84 has been discovered and more accurate measurements made of the abundances of the others.

RHODIUM.—A second isotope 101 has been discovered and its abundance estimated.

PALLADIUM.—The abundances of the numerous isotopes of this element have now been measured.

TELLURIUM.—A faint new isotope 120 has been detected.

BARIUM.—Three new isotopes 130, 132, 134 have been discovered.

CERIUM, NEODYMIUM.—In each of these elements two weak new isotopes have been discovered, but no figures for their abundances are yet available.

IRIDIUM, PLATINUM.—Accurate values of the abundance of the isotopes of these elements have been obtained.

A bibliography of the papers relating to this summary of recent work is appended.

The International Table of Stable Isotopes for 1937 is given in English, French and German, the respective atomic number (Z), mass number (M) and relative abundance (per cent.) of the isotopes of each element being given.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Proteolytic Activity of Barley Malt. S. Laufer. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 307–330.)—Infusions of malt were prepared by extracting the finely-ground sample for 2 hours with four times its weight of distilled water at 20° C., filtering, and, when the determination involved the measurement of viscosity, centrifuging. From the moisture-content of the malt and the sp.gr. of the infusion the amount of dry malt corresponding with 1 ml. of the infusion was calculated. Three methods were selected for the determination of the proteolytic activity. The first (Northrop and Hussey, *J. Gen. Physiol.*, 1923, **5**, 353; Lüers and Lőther, *Woch. Brau.*, 1935, **52**, 49) depends upon the measurement of the diminution of the viscosity of a gelatin solution resulting from the activity of a proteolytic enzyme, the time required to cause a definite percentage change in the viscosity of the substrate being inversely proportional to the amount of enzyme used (the "Arrhenius Q × T rule"). Granulated gelatin (U.S.P.) is brought to its iso-electric point of *p*H 4·7 by washing at 3° C. twice with twenty times its weight of water and twice with the same amount of $N/128$ acetic acid. The superfluous liquid is drained off by suction through muslin, and the semi-solid mass is evaporated on the water-bath to a concentration of 15 per cent., as ascertained by drying tests. The substrate is then treated with 0·5 per cent. of toluene and kept in an ice-chest. For the viscosity determination, 25 g. of the substrate are made up with 10 ml. of 0·2 M Sørensen's citrate buffer of *p*H 5·0 and water to 100 ml., and filtered to remove suspended matter. Ostwald viscometers, with an outflow rate of 60 to 80 seconds for 5 ml. of water at 40° C., were used, the outflow rate of the gelatin and malt mixture being about three times that of water. The filtered gelatin substrate (20 ml.) and the malt infusion were heated separately in the water-bath at 42° C. for 15 minutes, 5 ml. of the malt infusion were then added to the gelatin solution (zero time) and mixed thoroughly, after which 5 ml. of the mixture were pipetted rapidly into the viscometer, which had been warmed for 15 minutes in a glass water-bath at 40 ± 0·05° C. The first test should take place at 2 to 3 minutes after zero time, and measurements were made in frequent succession until a change of approximately 10 per cent. in the outflow rate was observed. To allow for changes in viscosity during measurement, one half of the outflow time was added to the time at which each measurement was taken, and this was regarded as the time of observation. The outflow times were plotted as ordinates against the times of observation, and the time required to effect a 10 per cent. change in the outflow time corresponding with zero time of observation (found by extrapolation) was read from the curve. The amount of enzyme required to reduce the initial viscosity by 10 per cent. in 10 minutes is suggested as the unit of proteolytic activity. In an experiment, 1 ml. of infusion corresponded with 0·2257 g. of dry malt, and a 10 per cent. change in initial viscosity was effected in 46 minutes. The activity of 100 g. of dry malt is therefore 96 units. In the second method a 2 per cent. solution of edestin is used as substrate, and the extent of proteolysis is determined by the Willstätter titration in alcoholic solution of the carboxylic groups liberated from the peptide linkages. The optimum *p*H of the mixture is 4·3 to 4·4. The edestin substrate contains 40 g. of edestin, 218 ml. of 0·2 *N* hydrochloric acid, 200 ml. of 0·3 *M* acetic acid and 0·14 *M* sodium acetate, per litre. Ten ml. of the substrate and 10 ml. of malt infusion, both at 37·5° C., are mixed and 2 ml. of the mixture are pipetted into 10 ml. of 96 per cent. alcohol in a 60-ml. flask. The mixture is titrated in the presence of 0·4 ml. of 5 per cent. alcoholic thymolphthalein solution with 0·05 *N* alcoholic potassium hydroxide solution to a distinct bluish-green colour; 20 ml. of hot alcohol are then added and the titration is continued to the appearance of the first bluish shade. The procedure is repeated with portions of the edestin-malt mixture after incubation for 24 hours at 37·5° C., 2 drops of toluene being added before incubation. The increase in the titration value is a measure of the proteolysis. The course of the reaction follows the Schütz–Arrhenius rule, *viz.* $x = K\sqrt{et}$, where x denotes the amount of protein digested (in ml. of 0·05 *N* potassium hydroxide solution), e the enzyme concentration, t the time of reaction, and K a velocity constant. In the third method the gelatin solutions used for viscosity measurements were used as substrates. The 15 per cent. gelatin solution (80 g.) was mixed with 20 ml. of Sørensen's citrate buffer of *p*H 5·0 and sufficient water to produce 100 ml. Ten ml. of this solution were mixed with an equal volume of malt infusion at 37·5° C., and the subsequent procedure used in the previous method was followed. The gelatin titration at zero time presented some difficulty, owing to the formation of curd and the occlusion of acids. A modified method of titration appears to be necessary. The results obtained by the three methods differ from sample to sample and show no definite relationship. Explanations of this, depending upon theories of enzyme composition and action, are suggested. No relationship was found between the proteolytic activity and the Lintner value (diastatic power) of the malt samples tested. In general, the 2-rowed varieties of malt showed a higher proteolytic activity than the 6-rowed varieties.

A. O. J.

Lactic Acid in Bordeaux Wines. J. Ribereau-Gayon and E. Peynaud. (*Ann. Falsificat.*, 1937, **30**, 339–344.)—For the determination of lactic acid in wines the acid was oxidised to acetaldehyde by the method of Espil (*Bull. Soc. Chim.*, 1935, **2**, 1286), and the acetaldehyde was titrated according to the method of Jaulmes and Espezel (*Ann. Falsificat.*, 1935, **28**, 325; Abst., ANALYST, 1935, **59**, 703). The details of the method are as follows:—Twenty ml. of wine are treated with 10 ml. of basic lead acetate solution (sp.gr. 1·32) and filtered. The sugars are removed from 10 ml. of the filtrate by adding 10 ml. of copper sulphate solution (100 g. per litre) and 10 ml. of milk of lime (100 g. of calcium hydroxide per litre), mixing, leaving 2 hours and filtering. Ten to 15 ml. of filtrate are collected and treated with an exactly equal volume of sodium carbonate solution (20 g. per litre), followed by filtration. To the filtrate is added an equal volume of *N*/5 sulphuric acid. Twenty ml. of this liquid (corresponding with 10/9 ml.

of wine) are put into a distillation flask with 2·5 ml. of N sulphuric acid, 10 ml. of manganous sulphate solution (50 g. per litre) and 40 ml. of water; a few pieces of pumice are added. The flask is connected with the distillation apparatus by a ground-glass joint carrying a capillary tube through which $N/200$ potassium permanganate solution falls from a dropping funnel at the rate of 1 drop per second on to the surface of the liquid. Boiling must be rapid and the addition of the potassium permanganate is not begun until the liquid has been boiling for several minutes, in order to remove the traces of alcohol. The distillate is received in a conical flask containing 20 ml. of a buffer solution of *p*H 7 and 20 ml. of a sodium bisulphite solution of about 1 g. per litre. The distillation is continued until the brown colour of the liquid in the flask indicates an excess of manganese oxide. The aldehyde in the distillate is then titrated by the method of Jaulmes and Espezel: oxidation of free sulphur dioxide in a medium of *p*H less than 2 and titration of the sulphur dioxide combined with the aldehyde with an $N/200$ iodine solution in a medium buffered to *p*H 8·5 by an alkaline solution of sodium borate. A volume of 0·5 ml. of iodine solution is subtracted to allow for the excess required to colour the starch indicator in an alkaline medium. One ml. of the iodine solution corresponds with 2·5 microgram-mols., or 0·23 mg., of lactic acid. The presence of manganous sulphate, rapid boiling regulated by pumice stone, and slow addition of the potassium permanganate are essential for accurate results; the error does not exceed 3 per cent. Tables show the results obtained with 28 white wines and 31 red wines analysed in March, 1937. The following table quotes the average results.

	Lactic acid, g. per litre	
Nature of the wine	Minimum and maximum quantities found	Average quantities
White wines	0·36, 2·45	1·04
Red wines of 1936* (6 months after harvest)	0·58, 1·07	0·77
Red wines, other years	1·31, 3·82	2·32

* Acid wines, from rather ripe grapes; it is certain that malo-lactic fermentation often occurs in the fermentation vat.

E. M. P.

Feeding Experiments with Canned Food Packed in Aluminium Containers. G. Lunde, V. Aschehoug and H. Kringstad. (*J. Soc. Chem., Ind.*, 1937, **56**, 334–339T.)—Although foods packed in aluminium containers absorb small quantities of aluminium and the amount may rise to 100 mg. per kg. after several years, this amount is not more than may be absorbed by cooking in aluminium utensils, and it appears to be quite harmless. Mice were fed on canned food containing about 0·05 mg. of aluminium per animal per day during the period of most rapid growth, and nothing abnormal about them could be detected, nor did they show any accumulation of aluminium. Rats fed on canned food containing about 0·4 mg. excreted the aluminium quantitatively, and their growth was normal. Fed thus to the fifth generation, they showed no injurious effects. Aluminium was determined in the lungs, heart, spleen, kidneys, liver, and muscle tissue, and in no instance had accumulation or retention occurred.

D. G. H.

Preferential Reduction of Certain Fatty Acid Groups during Hydrogenation of Natural Fats. D. A. Harper. (*J. Soc. Chem. Ind.*, 1937, **56**, 308–310T.)—Data given by the author in two (previous) papers (*vide infra*) and in a number of others where progressive hydrogenation of fats is recorded have been found amenable to analysis on a more quantitative basis than has so far been used, thus yielding additional information. The rate of hydrogenation is defined as the amount of acid (in the glycerides) reduced per unit time, *i.e.* per 100 mols. of reacting acid per unit time. Since the change in iodine value of the whole fat is a function of time, the rate can be expressed as the gram molecules of acid reduced per 100 mols. of the particular reacting acid per unit drop in iodine value. An example is taken from the hydrogenation of cod-liver oil (*vide infra*), iodine values 63, 35·8; oleic acid (mols.), 16·1, 10·6; stearic acid (mols.), 11·1, 16·6. Drop in iodine value 27·2, while 5·5 mols. of stearic acid have been produced. The amount of octadecenoic acid from which this was produced changed from 16·1 to 10·6 (arithmetical mean 13·4). Hence "rate," as defined above, is 5·5/27·2 × 100/amount of reactant acid = 5·5 × 100/27·2 × 13·4 = 1·5. This procedure has been applied to mixtures of cottonseed and linseed oils, to mixtures of cottonseed and soya oils, and to rape oil (ANALYST, 1935, **60**, 839). Selective effects are seen to be well developed in a simple fat when di- and mono-unsaturated acids of the C_{18} series are the only acids present (apart from saturated acids), but in a more complex fat the preferential reduction of the di-unsaturated acids to the mono-unsaturated is not nearly so well developed. The corresponding esters, however, show the selectivity restored. There is also variation in selection according to the molecular weight of the reduced acid. The octadecenoic to stearic reduction appears to be slowest, and the docosenoic fastest. The extent of these preferential reductions is somewhat smaller than with the diethenoid and monoethenoid acids, but in the esters the preference is completely reversed in the C_{22} and C_{18} series. Increase of temperature of reduction causes a greater degree of selection with linolic and oleic derivatives. All the rates tend to become equal at low iodine values. D. G. H.

Tin-content of English Canned Fruits and Vegetables. W. B. Adam and G. Horner. (*J. Soc. Chem. Ind.*, 1937, 56, 329–334T.)—About 1300 analyses have been carried out over a period of 10 years to determine the proportion of tin found in canned fruits and vegetables in plain and lacquered containers. The contents of the tin were first separated into liquid and drained-solid portions, and samples were taken in proportion to their weights. The sample was digested with sulphuric and nitric acids in a Kjeldahl flask. The fine crystalline precipitate which often formed on the destruction of the organic matter sometimes contained tin, apparently as metastannic acid; it was removed from the diluted solution, washed and fused in a silver crucible with a little sodium hydroxide, the residue was dissolved in water, and the solution was acidified with hydrochloric acid and added to the original solution, which was then neutralised with ammonium hydroxide. The volume was adjusted to 400 ml., about 20 ml. of conc. hydrochloric acid were added, and hydrogen sulphide was passed at 95° C. for an hour. Digestion at 95° C. was continued for 2 to 3 hours, and the precipitate was then collected and washed with ammonium acetate solution and acetic acid. The precipitate and

paper were extracted three times with ammonium sulphide solution saturated with sulphur, pulped with hot water, and filtered. The tin was then precipitated with acetic acid, digested for 2 hours at 95° C., allowed to stand overnight, filtered off and washed. The precipitate and paper were ignited in a weighed crucible at a low heat for 3 to 4 hours, and finally the temperature was increased for a few minutes, after which the crucible was cooled and weighed. A comparison of plain and lacquered cans showed that for fruits (gooseberries, raspberries, red currants, loganberries, blackcurrants, Victoria plums and damsons) there were seldom more than 100 mg. of tin per kg. in the fruit in plain cans, so that although the figure was considerably less in the lacquered cans, it is not suggested that plain tins should not be used for this class of fruit. Fruits and vegetables in lacquered cans, even after long storage, hardly ever contained more than 40 mg. of tin, and if the seams and expansion rings of the tin were protected by spray lacquering, solution of tin was virtually eliminated. Tin was dissolved by the fruit fairly rapidly during the short time in which free oxygen remained, but after that the rate of solution was very slow. When cans were stored at 72° and 95° F. the tin-content (on the average) exceeded that in the cans stored at normal temperatures by 46 and 170 per cent., respectively. The proportion of tin in the drained solids was about twice that found in the syrups. The *p*H was not of great importance, nor did it matter whether water or sugar syrup was used as a covering liquid; further, the state of ripeness of the fruit had no appreciable effect on the tin-content. Some vegetables contain substances, probably amino compounds, which accelerate solution of tin. For this reason in this country dwarf beans and spinach are always packed in lacquered cans. The slight metallic tang imparted by the absorbed tin to asparagus appears to be liked by the public, and asparagus is therefore canned in plain tins, but the result is not satisfactory, about 300 mg. of tin per kg. dissolving in 1 to 2 years. Rhubarb also attacks tin coating severely.
D. G. H.

Component Acids and Glycerides of Partly Hydrogenated Marine Animal Oils. I. General Review of the Analytical Procedure Employed. D. A. Harper, T. P. Hilditch and J. T. Terleski. (*J. Soc. Chem. Ind.*, 1937, **56**, 310–315T.)—The component acids of marine animal oils vary in molecular size from C_{14} (or even C_{12}) to C_{22} or C_{24}, and in unsaturation from mono- to penta- or hexa-ethenoid. They thus present a more complex mixture of mixed glycerides than is found in oils studied previously by means of hydrogenation (*cf.* ANALYST, 1935, **60**, 839), so that certain modifications are necessary both in the analytical work and in the arithmetical interpretation of data. Unsaponifiable matter should be removed before conversion of the fatty acids into methyl esters. In order to obtain adequate separation, numerous refractionations of the primary fractions of the distilled methyl esters of both "solid" and "liquid" acids are necessary. Details of the complete ester fractionation data are given for a lightly hydrogenated whale oil (iodine value 88·6) and a more completely hydrogenated cod-liver oil (iodine value 24·8), to illustrate the procedure. Since a somewhat large proportion of the ester fractions is liable to contain two saturated esters and unsaturated esters derived from two groups in the homologous series of fatty acids, the equivalent of the saturated esters present after removal of all unsaturated esters by oxidation with potassium permanganate, is determined. If the iodine value of the original fraction exceeds 40, it is usually necessary to repeat the process once or twice before all unsaturated components have been converted into acidic products. Details of the methods of calculation involved are given. The deviation from the mean values obtained for each homologous group of acids affords evidence of the degree of accuracy reached, since each analysis is in effect that of a distinct fat. (See also following abstracts.) D. G. H.

II. Antarctic Whale Oil. T. P. Hilditch and J. T. Terleski. (*J. Soc. Chem. Ind.*, 1937, **56**, 315–322T.)—The whale oil used was a 3-gallon sample of the No. 0 grade from the 1933–34 whaling season in the Antarctic, and had saponification equivalent 286·5 and iodine value 109·3, and contained 0·53 per cent. of free fatty acids. The neutralised oil was hydrogenated at 170 to 180° C. to products with iodine values 88·2, 70·7, 48·8, 28·2, and 11·9, and each of these fats and the original oil were examined to determine the approximate percentages of component fatty acids, tabulated as molar percentages. The mixed fatty acids of the oil consisted of myristic, 9; myristoleic, 4; palmitic, 17; palmitoleic, 17; stearic, 2; C_{18} unsaturated (mean unsaturation −2·6H), 35; C_{20} unsaturated (−5·6H), 12; C_{22} unsaturated (−9H), 4, as molar percentages. The small proportion of C_{22} and moderate proportion of C_{20} acids are characteristic. A complex mixture of glycerides is present, but since there are only 16 to 20 per cent. of combined C_{20} and C_{22} acids, almost half probably consists of glycerides containing only acids of the C_{18}, C_{16} and C_{14} series. Hydrogenation is partly selective; polyethenoid C_{22}, C_{20} and C_{18} acids tend to become monoethenoid derivatives before any of the respective saturated acids are produced in quantity, but monoethenoid derivatives of one group begin to change to saturated derivatives before all polyethenoid unsaturation in other groups has disappeared. Since the formation of fully-saturated glycerides is dependent on the first reduction of poly- to mono-ethenoid compounds, and subsequently on the transformation of tri- to di-, and di- to mono-unsaturated glycerides by successive stages, they do not increase rapidly until a comparatively low iodine value has been reached. (See also preceding abstract.) D. G. H.

III. North Sea Cod-liver Oil. D. A. Harper and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1937, **56**, 322–329T.)—The cod-liver oil used had iodine value 177·7, and was hydrogenated to fats with iodine values 100·3, 77·0, 63·0, 48·8, 35·8, 24·8, and 14·3. These fats were examined in the same manner as whale oil (*cf.* preceding abstract). The oil contained mixed fatty acids of the following approximate molar composition: myristic, 2; myristoleic, 2; palmitic, 14; palmitoleic, 10; stearic, 1; C_{18} unsaturated (−3·3H), 26; C_{20} unsaturated (−5·5H), 25; C_{22} (−7·4H), 20; C_{24} unsaturated, less than 1 per cent. The high content of C_{22} and somewhat lower proportion of palmitoleic acid are characteristic. A very complex mixture of glycerides is present and, since 45 per cent. of the acids are C_{20} and C_{22}, most glyceride molecules will contain at least one acid group of these series. Selective hydrogenation takes place as follows: to 80 units iodine value fall there is reduction of polyethenoid unsaturation, followed by the acids of the C_{18} series rapidly reaching monoethenoid unsaturation, and subsequent production of stearo-glycerides. In the C_{20} and C_{22} series, although the mean unsaturation continues to decrease, action becomes less marked as the iodine value of the fat decreases, and complete reduction to not more than monoethenoid unsaturation is not reached till the iodine value is very small, reduction of di- to mono-unsaturation, and mono-unsaturation to saturation taking place side by side. The production of fully-saturated glycerides in the first half of hydrogenation is negligible, but thereafter accelerates and becomes very rapid when the iodine value of the fat is small. (See also preceding abstracts.) D. G. H.

Detection of Gums in Certain Food Products. F. L. Hart. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 527–534.)—The following methods are applicable to the types of food indicated. *Agar-agar in Mayonnaise.*—Treat 50 to 75 g. of mayonnaise with 40 ml. of hot water, heat to 70° C., add 10 ml. of trichloroacetic acid solution (50 per cent. w/v) and maintain at 65 to 70° C. for 10 minutes or until the emulsion breaks. Transfer the mixture to an 8-oz. centrifuge bottle, cool, add 30 to 40 ml. of toluene and centrifuge for 15 or 20 minutes at 1,200 r.p.m. Remove as much as possible of the aqueous layer and filter it into an 8-oz. centrifuge bottle. Add 1 ml. of trichloroacetic acid solution and re-filter if necessary. Mix the filtrate with twice its volume of acetone and, when the precipitate has coagulated, centrifuge the mixture, discard the liquid and wash the precipitate by centrifuging with 70 per cent. acetone. To the washed residue add 30 to 50 ml. of water and 2 or 3 drops of acetic acid, mix well and filter if necessary. To the filtrate add alcohol, one volume at a time. Agar is precipitated by four volumes of alcohol; if no precipitate occurs with five volumes of alcohol after two hours, the absence of gums and dextrin is indicated. This method will detect 0·14 g. of agar in 50 g. of mayonnaise. The procedure has not been tried for other gums.

Added Gums in Cheese and Ice-cream.—Thoroughly extract 100 g. of warmed cheese by decantation with petroleum spirit. Warm the de-fatted cheese to remove residual spirit, add 100 ml. of hot water and heat to boiling-point, stirring continually. Add 4 or 5 drops of ammonia, mix thoroughly, transfer to a centrifuge bottle, neutralise to litmus paper with conc. acetic acid, and add a few drops in excess. Centrifuge for 10 to 20 minutes and separate the liquid by decantation. (If the mixture does not separate into distinct layers upon centrifuging, the aqueous gum solution is separated by filtration under reduced pressure through a coarse filter.) Evaporate the liquid to about 40 ml. (disregarding any precipitate formed during concentration), add 10 ml. of trichloroacetic acid solution and maintain the temperature at 70° C. until the precipitate coagulates. Cool and filter. Add four volumes of alcohol and allow the mixture to stand for two or three hours. A precipitate indicates the presence of gums. Separate the precipitate by centrifuging and wash it with 70 per cent. alcohol. Remove occluded sugars by dissolving the washed residue in the minimum amount of hot water and re-precipitate with four volumes of alcohol and a few drops of acetic acid. Dissolve the precipitate in the minimum amount of hot water, evaporate to 5 ml., add an equal volume of conc. hydrochloric acid, boil for 30 to 60 seconds, and add 2 or 3 crystals of phloroglucinol. A deep amber or cherry-red colour confirms the presence of gums. For uncreamed cheese the extraction with petroleum spirit is omitted. This method was proved capable of detecting 0·1 per cent., and even less, of the following gums added to gum-free cheese:—agar-agar, tragacanth, India gum, karaya, locust-bean gum and gum arabic. Positive results were obtained also with the commercial gums Neogell, Hygell and Tragon A. Gelatin and sour cream protein (pseudo-gelatin) do not interfere with the test. The method was applied successfully to vanilla ice-cream. With fruit ice-cream the pectin present may interfere.

Agar-agar in Canned Chicken.—From the canned meat separate the gel, which contains agar, collagen, soluble protein, and meat extractives. Dissolve 25 to 50 g. of the gel in 25 ml. of water. Filter through a coarse mat of asbestos in a Gooch filter, adjust the filtrate to *p*H 2 to 2·5 (reddish-yellow with thymol blue) by the addition of a slight excess of hydrochloric acid and back titration with *N* sodium hydroxide solution, add 0·1 g. of pepsin, and digest for 1 hour at 38° C. or overnight at room temperature. Add to the digest a weighed amount of trichloroacetic acid sufficient to make a 10 per cent. solution, warm to coagulate the precipitate, cool and filter. To the filtrate add twice its volume of acetone, and from this point follow the procedure for the detection of agar in mayonnaise. Coagulation of the final alcohol precipitate may be hastened by the addition of a few mg. of alum.

Gum in Tomato Products (Catsup, Purée, Consommé).—Since tomatoes contain pectin the separation of gum is difficult, and it is advisable to carry out the process simultaneously upon a sample of gum-free tomato product. In an 8-oz. centrifuge bottle make up 50 g. of the sample to 5 oz. with cold water, shake thoroughly and allow to stand for several hours with occasional shaking. Centrifuge the mixture, filter off 100 ml. of the supernatant liquid through a Buchner funnel, and evaporate the filtrate to about 30 ml. Cool and add 10 ml. of trichloroacetic acid solution (50 per cent. w/v), warm to 70° C., centrifuge the mixture for 10 minutes and filter. To the clear filtrate add 5 times its volume of 96 per cent. alcohol, allow the precipitate to coagulate, adding a few mg. of alum if necessary, centrifuge for 10 to 15 minutes, decant the supernatant alcohol, wash the residue once by decantation with alcohol, and filter. Dissolve the precipitate in not more than 30 ml. of water, filter with the aid of suction if necessary, cool below 25° C., and add 3 to 5 ml. of 10 per cent. sodium hydroxide solution diluted to 50 ml. with cold water. Allow the mixture to stand in ice or running water for 15 minutes, filter by suction, neutralise to phenolphthalein, add 1 or 2 drops of glacial acetic acid, and evaporate to 30 ml. An immediate precipitate indicates the presence of gums. A slight cloudiness due to pectic bodies is disregarded. Confirm the presence of gums by hydrolysis of the precipitate with dilute acid and subsequent colour tests. Pectin is hydrolysed to reducing sugars (arabinose and galactose), but these do not give the resorcinol test until they have stood for half-an-hour. A. O. J.

Turtle Oils from Ceylon. (*Bull. Imp. Inst.*, 1937, 35, 316–318.)—The following 4 samples were examined: (1) Carapace oil of leathery turtle (stated in *Ceylon J. of Science*, 1930, [B], 6, 45, to be *Dermochelys coriacea*, known locally as "Dhara kasbava,") rendered over fire in a zinc bath-tub; it was a reddish-brown liquid, containing a large quantity of light brown stearine and having a strong fishy odour. When melted the oil was clear and very dark reddish-brown. (2) Dhara kasbava oil from *Dermochelys coriacea*; a golden-brown liquid, containing a very large quantity of yellowish-brown stearine and having a strong fishy and rancid odour. When melted the oil was clear. (3) Green turtle or Perr Amai oil from *Chelonia mydas*; a golden-brown liquid, containing a large quantity of yellowish stearine and possessing a fishy odour. A very small amount of "dirt" (albuminoid matter) was present. When melted the oil was very slightly cloudy. (4) Kanga mattaya oil from *Lepidochelys olivacea*; an orange semi-solid oil with a fishy odour. When melted the oil was very slightly cloudy. The results obtained are shown in the table, which quotes also previously recorded figures.

PRESENT SAMPLES

	Leathery turtle: Carapace oil	Dhara kasbava (*Dermochelys coriacea*)	Green turtle (*Chelonia mydas*)	Kanga mattaya (*Lepidochelys olivacea*)
Moisture, per cent.	0·1	0·2	0·1	0·2
Sp.gr. at 100/15° C.	0·8696	0·8671	0·8644	0·8710
Refractive index, n_D^{40}	1·4650	1·4635	1·4591	1·4698
Acid value	1·6	17·1	1·1	0·4
Saponification value	197·5	199·6	207·6	191·5
Iodine value	98·9*	103·8*	68·2*	148·7†
Unsaponifiable matter, per cent. ..	3·3	1·8	0·5	1·3

* Wijs, ½ hour. † Wijs, 1 hour.

RECORDED FIGURES

	Leathery turtle (*Dermochelys schlegelii*) Japan	Green turtle (*Chelonia mydas*)			"Turtle"		
		(1)	(2) Panama	West African	Eleven commercial samples	Ceylon	Egyptian
Moisture, per cent. ..	—	—	—	—	—	—	—
Sp.gr.	0·9252 at 15/4° C.	0·9335 at 15/15° C.	0·9205 at 15/15° C.	0·9112 at 40/40° C.	0·914 to 0·919 at 25° C.	—	—
Refractive index, n_D^{40}	1·4753 at 20° C.	1·4769 at 20° C.	—	1·4599	1·4658 to 1·4715 at 20° C.	1·459	1·4585
Acid value	2·0	1·17	0·56	2·0	—	1·45	—
Saponification value	181·3	193·8	213·5	209	197–210	209·5	213
Iodine value ..	128·1	127·4	61·5	64·6	89–97	65·5	57·2
Unsaponifiable matter, per cent...	—	—	0·45	0·6	—	0·65	—

(See also W. Lee, ANALYST, 1935, **60**, 650.) E. M. P.

Differential Action of some Aromatic Aldehydes on Morphine and Hydroxydimorphine. B. Drevon. (*J. Pharm. Chim.*, 1937, **26**, 292–299.)—A new colour reaction for morphine and hydroxydimorphine is obtained by heating these alkaloids in solution in conc. hydrochloric acid with conc. hydrochloric acid solutions of aromatic aldehydes in which the aldehyde group is directly linked to the benzene nucleus. The reaction is not as sensitive as those of Marquis and of Pesez (*J. Pharm. Chim.*, 1937, **25**, 504) for morphine or the author's aceto-sulphuric reaction (*J. Pharm. Chim.*, 1935, **22**, 97; Abst., ANALYST, 1935, **60**, 707) for the micro-determination of hydroxydimorphine. The morphine was in the form of the officinal hydrochloride; the hydroxydimorphine was obtained by oxidising morphine hydrochloride with potassium ferricyanide in alkaline solution (Drevon, *Thèse Dip. Sup. de Pharm., Lyon*, 1931), distilling the alkaloid *in vacuo* from its ammoniacal solution, and fractionally recrystallising the trichloroacetate (particularly to free it from iron), and also by the biological method (Leulier, *C. R. Soc. Biol.*, 1935, **118**, 882), the colourless juice of *Polyporus lacteus* Fr. being used as oxidising agent. The strength of the aldehyde solutions was 0·3 per cent. when possible; otherwise, cold saturated solutions were employed. The mixture of alkaloid and aldehyde solutions was heated on a boiling water-bath for 3 to 10 minutes. The only acyclic aldehyde to give a colour was formaldehyde, which yielded a yellow colour with morphine and an orange colour with hydroxydimorphine. The reaction is not given by aldehydes in which the aldehyde group is linked to a five-membered oxygen-containing ring, or in which the aldehyde group forms part of an oxygenated ring, such as the "pseudo-aldehyde" group of some aldoses (glucose). The table shows the colours obtained with different reagents:

Substance examined	Reaction obtained		
	Blank	Morphine	Hydroxydimorphine
Phenol	No colour	No colour	No colour
Benzyl alcohol			
Benzaldehyde	Pink	Dirty olive green	Pure green
Benzoic acid	No colour	No colour	No colour
o-Nitrobenzaldehyde	Straw yellow	Golden yellow	Deep green
o-Hydroxybenzyl alcohol	No colour	No colour	No colour
Salicylaldehyde ..	Orange-pink, with turbidity	Onion-skin red, with turbidity	Blue-green, with turbidity, turning blue after long heating
Salicylic acid	No colour	No colour	No colour
Anisaldehyde ..	Very pale pink	Violet-pink	Greenish-blue
Pyrocatechol	No colour	No colour	No colour
Resorcinol			
Hydroquinone			
Orcinol ..			
Pyrogallol			
Phloroglucinol			
Gallic acid			
Protocatechuic aldehyde	Colourless	Violet-pink	Green
Cinnamic alcohol ..	No colour	No colour	No colour
Cinnamic aldehyde ..	Colourless, then yellowish	Dichroic violet	Greenish
Cinnamic acid	No colour	No colour	No colour
Vanillin	Light yellow	Violet-red	Green
Piperonal	Bordeaux red, with turbidity	Dichroic red-brown	„
Piperic acid	No colour	No colour	No colour
Coumarin			
Furfural			

E. M. P.

Determination of Iodine in Thyroid Gland Preparations. J. C. De Jong. (*Pharm. Weekblad*, 1937, **74**, 1429–1437.)—To a solution of 200 mg. of sample in 5 ml. of warm 4 N sodium hydroxide solution are added in succession 200 mg. of talc, which is distributed thoroughly by shaking, 50 ml. of 4 per cent. potassium permanganate solution, and 25 ml. of 4 N sulphuric acid. The mixture is heated in a 300-ml. Erlenmeyer flask on which is a mark indicating 75 ml., until frothing starts, and it is then allowed to boil gently for 5 minutes. It is then cooled, an excess of sodium bisulphite (*e.g.* 3 g.) is added to destroy the excess of permanganate, after which the mixture is boiled with 3 ml. of a 0·1 *N* solution of silver nitrate until the excess of sulphur dioxide is itself removed. As a result of these operations the iodate produced by the action of the permanganate is converted into silver iodide. The solution is boiled with 15 ml. of 50 per cent. nitric acid, and filtered when cold on a hard filter, the first portion of the filtrate being re-filtered; the residue on the filter is washed until the filtrate is neutral to litmus paper. The precipitate is then washed back into the original flask, the volume is made up to the 75 ml., and 5 ml. of dilute sulphuric acid and 10 ml. of freshly-prepared bromine water are added to convert the silver iodide into silver bromide and the iodine into iodate. The excess of bromine is removed by boiling, and the cool solution is titrated with 0·01 *N* sodium thiosulphate solution (1 ml. ≡ 0·212 mg. of iodine) in the presence of 5 ml. of a 1 per cent. solution of phenol, a crystal of potassium iodide and starch solution. It is shown that under the conditions described the influence of the iodine on the solubility of silver bromide or silver chloride, of light on the precipitated silver iodide, and of the solubility of the silver iodide itself are negligible; also, that oxidation in the manner described is preferable to fusion with alkali (as recommended by the Dutch Pharmacopoeia, Ed. V), or to the use of an alkaline oxidising agent. Results obtained with "synthetic" preparations containing known quantities (0·25 to 10 ml.) of 0·005 *N* iodate solution gave maximum errors of −0·05 to +0·15 ml. of 0·01 *N* sodium thiosulphate solution. The iodine-contents of 14 commercial samples of thyroid preparations ranged from 0·302 to 0·837 per cent. J. G.

Biochemical

Deuterium as an Indicator in the Study of Intermediary Metabolism. D. Rittenberg and R. Schoenheimer. (*J. Biol. Chem.*, 1937, 121, 235–253.)—A consideration of the reactions by which deuterium may enter from the water of the body fluids into organic combination indicates that the formation of cholesterol in the animal body is a more fundamental process than has been supposed hitherto, and involves the coupling of a large number of small molecules. Experiments, carried out *in vitro*, on the exchange of the hydrogen of palmitic acid and cholesterol with that of heavy water, indicate that neither of the two compounds contains any slowly exchangeable (semi-labile) hydrogen. The heavy water-content of mice was raised by injection of D_2O to 1·5 per cent. and kept at that level for periods up to 98 days. Groups of mice were killed at intervals, and the fatty acids and cholesterol were isolated. The fatty acids were separated into the unsaturated and saturated acids, and from the latter palmitic and stearic acids were isolated. As in previous experiments, the deuterium-content of the total fatty acids increased with time and reached a constant value. The complete data indicate a half-lifetime of about 5 to 9 days for the fatty acids. The deuterium-content of the saturated acids was always higher than that of the unsaturated acids; stearic and palmitic acids had about the same deuterium-content. The deuterium-content of the cholesterol rose to one half that of the body fluids, but the rate of increase was less than that of the fatty acids and indicated a half-lifetime of about 15 to 25 days. Cholesterol was also isolated from chick embryos which had developed in eggs containing heavy water. It did not contain deuterium; this fact is held to prove that there is an absence of an *in vivo* exchange which is not reproducible *in vitro*. During the developmental period of hens' eggs there occurs neither synthesis nor degradation of cholesterol. The high deuterium-content of the cholesterol in mice suggests that in mammals it is prepared by the coupling of a large number of small molecules. S. G. S.

Estimation of Deuterium Oxide and Water Mixtures. W. H. Patterson. (*J. Chem. Soc.*, 1937, 1745–1746.)—The critical solution temperatures and the mutual miscibility temperatures of mixtures of deuterium oxide, water and phenol have been investigated and correlated with direct determinations of density to provide a rapid method of estimating the deuterium oxide content of water when the amount available is small. The critical solution temperature of water-phenol is 66·0° C., and no change can be noted with variations of phenol-content between 34·2 and 37·8 per cent. (Carrington, Hickson and Patterson, *J. Chem. Soc.*, 1925, **127**, 2544). Timmermans and Poppe (*Compt. rend.*, 1935, **201**, 524) give 12·25° C. as the rise of critical solution temperature when deuterium oxide replaces water, and Hall, Wentzel and Smith (*J. Amer. Chem. Soc.*, 1934, **56**, 1822) found a rise of 5·58° C. when using water containing 47·2 per cent. (molar fraction 0·466) of deuterium oxide. Mixtures were made by diluting the original sample, stated to contain 99·6 per cent. of deuterium oxide and to have a density $d_{4^\circ}^{20^\circ}$ of 1·10495 (the density found after the tube had been opened several times was 1·1043), and the densities of the mixtures were determined by means of a pyknometer of capacity 0·4882 ml. made by blowing a bulb on a tube and drawing out the ends into capillaries to give a V-shape. Mutual miscibility curves were constructed for four dilutions, the maxima of these curves giving the critical solution temperatures. The results were as follows:

D_2O per cent.	Molar fraction	Density $d_{4^\circ}^{20^\circ}$	C.S.T.	Critical concentration of phenol (per cent.)
99·6	0·996	1·1043	78·2	31·0
66·76	0·644	1·0678	74·4	32·5
52·65	0·500	1·0506	72·2	33·0
19·53	0·179	1·0170	68·6	35·0

The results show that the densities have a slight negative deviation from the linear. The critical concentration of phenol changes progressively from 36·1 with water to 31·0 with deuterium oxide. Otherwise the curves are similar and enable concentrations other than critical to be used for the estimation. The rises in critical solution temperature occurring when water is replaced by alleged 99·6 per cent. deuterium oxide and by 52·65 per cent. deuterium oxide are 12·2° C. and 6·2° C., respectively. For the latter equimolar mixture a rise of 1·24° C. represents 0·1 molar fraction of deuterium oxide. This figure enables an approximate analysis to be made. For intermediate concentrations a slight increase is necessary. The figure calculated from the results of Hall, Wentzel and Smith (*loc. cit.*) is 1·25° C.

This variation, which needs more accurate determination if results correct to 1 per cent. are required, is probably due to the fact that only three curves are concerned with two-component systems, *viz.* phenol with 100 per cent. deuterium oxide, with 52·65 per cent. deuterium oxide (corresponding with HDO), and with 100 per cent. water; all other curves represent three-component systems.

A. O. J.

Composition of the Liver Fats of some New Zealand Farm Animals. T. P. Hilditch and F. B. Shorland. (*Biochem. J.*, 1937, 31, 1499–1515.)—The "glyceride" and "phosphatide" constituents of the liver lipoids of the ox, cow, pig and sheep have been studied. The usual method of the phosphatide-glyceride separation has been found to be incomplete, owing to the low solubility of the di- and tri-saturated glycerides (present in typical animal fats) in acetone. A correction has been introduced by the use of a third or mixed phosphatide-glyceride fraction. The main error involved was the increase of the apparent content of saturated acid in the phosphatide fraction at the expense of the glyceride fraction. The error for the individual fatty acids was usually small, but the uncorrected palmitic acid content of cow's liver glyceride was 29·8 per cent. (mol.), as compared with the corrected figure of 34·7 per cent. (mol.). The non-phosphatide fatty acids of the liver resembled those of the corresponding depot fats. The former were distinguished, however, by the presence of 5 to 10 per cent. (mol.) of C_{20} to C_{22} highly unsaturated acids, the proportions in both being greater than in the depot fats. The similarity between these two types of fat is further indicated by the occurrence of small quantities of hexadecenoic acid—3 to 4 per cent. (mol.)—which has not been reported previously, together with the relatively constant 25 to 30 per cent. (mol.) of palmitic acid of the liver glyceride. The liver phosphatides are characterised by an increased proportion of stearic, C_{20} and C_{22} unsaturated acids together with diminished amounts of hexadecenoic acid, as compared with the corresponding liver glycerides, which also tend to contain acids of higher molecular weight. Linolic acid was not detected in the fatty acids from cow- and ox-liver, but traces were found in those from the pig and sheep. Linolenic acid was also found in the sheep-liver fatty acids.

S. G. S.

Amount of Iodine in Blood. E. J. Baumann and N. Metzger. (*J. Biol. Chem.*, 1937, 121, 231–234.)—The generally accepted figure of 8 to 13 micrograms of iodine per 100 ml. of blood is stated to be 100 per cent. too high. Analyses of blood from twenty normal persons gave, for males, 3·0 to 4·4 micrograms per 100 ml. (average 3·5), and for females, 2·3 to 3·0 micrograms per 100 ml. (average 2·6). The difference between the iodine contents of blood of the different sexes is outside the limits of error of the method used and is significant. In the case of patients suffering from Graves' disease the iodine content of the blood rose to 46 micrograms per 100 ml. The ingestion of 0·5 g. of iodine as potassium iodide caused a rise in the iodine in the blood from 3·4 micrograms to 59·4 and 6·6 micrograms after 48 and 96 hours, respectively. The method of determination consists in measuring 10 ml. of blood into a 500 ml.-flask with an interchangeable ground glass joint. To this 14 to 15 ml. of 100 per cent. chromic acid solution (250 g. of CrO_3 and 150 ml. of water) are added, and then cautiously 60 ml. of conc. sulphuric acid, the flask being cooled in an ice-bath during the addition of the first 25 ml. The flask is heated to 180° C., with shaking, then cooled, and 15 ml. of distilled water are added. The flask is again heated to 180° C. in an air-bath and cooled again, and finally 100 ml. of distilled water are added. This solution is now distilled in the Leipert (*Biochem. Z.*, 1933, **261**, 436) apparatus or in that described by Trevorrow and Fashena (*J. Biol. Chem.*, 1935, **110**, 29; 1936, **114**, 351). Ten ml. of distilled water and 0·3 ml. of 10 per cent. potassium hydroxide solution are measured into the receiver, which is attached to the condenser. Fifteen g. of oxalic acid are added to the digestion mixture, and the flask is at once connected with the receiver and heated cautiously at first while the violent evolution of carbon monoxide and dioxide is in progress, and then more vigorously until 50 ml. have distilled over. During the entire distillation a slow stream of air is passed through an alkali wash-bottle and the distillation apparatus. The distillate is concentrated, neutralised, oxidised with bromine and titrated with 0·001 *N* sodium thiosulphate solution, as described previously (*J. Biol. Chem.*, 1932, **98**, 405). A recovery of 92 to 100 per cent. was obtained with standard iodine solutions, from 92 to 95 per cent. with thyroxine and di-iodotyrosine, and 98 to 100 per cent. from blood with added iodine. S. G. S.

Action of Sunlight on Milk. L. Buruianä. (*Biochem. J.*, 1937, **31**, 1452–1458.)—The action of sunlight on milk causes oxidation of the unsaturated fat and oxidation of the ascorbic acid present by catalytic dehydrogenation. The oxidation of the unsaturated fat is independent of the decolorising of methylene blue, but the reduction of the dye is aided by the oxidation of this portion of the fat, which produces anaerobic conditions in the milk by using up the dissolved oxygen and thus allowing the second phenomenon to appear. The dehydrogenation of the ascorbic acid is responsible for the decolorising of the methylene blue which serves as a hydrogen acceptor. When all the ascorbic acid has been oxidised, the colour of the methylene blue is restored if air or oxygen be admitted. The determination of the substances oxidisable by iodine, before and after exposure to sunlight, can be used to evaluate the vitamin *C* content of milk. The results obtained by this method agree well with those obtained by direct titration with 2:6-dichlorophenolindophenol by the method of Schlemmer *et al.* (*Biochem. Z.*, 1932, **254**, 187). The rate of reduction of methylene blue on exposure of the milk to sunlight does not give quantitative information about the ascorbic acid content, because this rate depends on the amount of unsaturated fat present. The milks examined, with the exception of mare's milk, did not contain reduced glutathione; mare's milk is being studied further. S. G. S.

Isolation of Crystalline Vitamin *A*. H. N. Holmes and R. E. Corbet. (*J. Amer. Chem. Soc.*, 1937, **59**, 2042–2047.)—Crystalline vitamin *A*, in the form of pale yellow needles, has been obtained from the liver oils of three different species of fish, *Stereolepsis ishinagi*, Atlantic mackerel, and one designated, for commercial reasons, "No. 1364." The oil was saponified cold in the presence of isopropyl alcohol and nitrogen, the soap was dissolved in water, and the solution was then extracted with petroleum spirit. The petroleum spirit extract was evaporated to a low bulk on the water-bath, and the concentrated solution was transferred to crystallising dishes which were placed in a vacuum desiccator and dried. The residue was dissolved in methanol, filtered cold, and transferred to a nitrogen-filled bottle for freezing. The bottle was kept for several hours in a bath of ice and salt, and any precipitate formed was discarded. The solution was kept for several days in contact with solid carbon dioxide, and any precipitate formed was filtered off. The filtrate was concentrated, transferred to a nitrogen-filled bottle and again left in contact with solid carbon dioxide. If a precipitate appeared, it was filtered off and 1 per cent. of water was added and the solution again crystallised. The crude crystals were dissolved in absolute methanol, cooled under nitrogen and frozen again by means of solid carbon dioxide, a few drops of water being added if necessary. About 30 per cent. of the original vitamin *A* in the oil was obtained in the crystalline form. The crystals from the three species of fish melted between 7·5° C. and 8° C. The extinction coefficient was found to be $E^{1\%}_{1\,\mathrm{cm}}=2100$, equivalent to a molecular extinction coefficient of 60,000. A biological assay of the crystals indicated between 2,265,000 and 3,400,000 international units per gram. The molecular weight of the crystals from the ishinagi oil was found to be 294 (Karrer's formula requires 286), and ultimate analysis gave 83·28 per cent. of carbon and 10·44 per cent. of hydrogen (Karrer's formula requires 83·84 per cent. of carbon and 10·56 per cent. of hydrogen). S. G. S.

Vitamin *P*. S. S. Zilva. (*Biochem. J.*, 1937, **31**, 1488.)—In a previous communication (*Biochem. J.*, 1937, **31**, 915) the author reported that a daily dose of 1 mg. of "citrin" or hesperidin administered to guinea-pigs on a scorbutic diet did not, as claimed by Szent-Györgyi (*Nature*, 1937, **139**, 326) prolong their life in consequence of the "vitamin *P*" activity regulating the vascular permeability. As the colleagues of Szent-Györgyi report that only animals receiving a suitable diet respond to "vitamin *P*" activity, the present author records the previous history and diets of his experimental animals and states that the negative results obtained by him cannot be traced to the unsatisfactory state of the animals, but that the explanation must be sought in another direction. S. G. S.

Bacteriological

Growth of *Streptococcus pyogenes* in Milk Stored at Atmospheric Temperatures. E. J. Pullinger and A. E. Kemp. (*J. Hyg.*, 1937, 4, 527–538.) —*Streptococcus pyogenes* (or *S. haemolyticus*) grows readily in sterilised milk and at 18 to 20° C. may multiply enormously in 24 hours. This growth, however, does not occur in pasteurised milk, particularly in commercial pasteurised milk and in raw milk, partly, it is suggested, owing to the bacteriostatic action of the milk, partly to competition with saprophytic micro-organisms, and partly to the inhibiting effect of their metabolic products. Experiments are described in which the rate of multiplication of three strains of *S. pyogenes*—(1) an old laboratory strain, (2) a freshly-isolated strain from human tonsilitis, and (3) a freshly-isolated strain from the udder of a cow naturally infected with this organism—was determined. These experiments, the results of which are tabulated, show that in pasteurised and raw milk there is no multiplication of *S. pyogenes* in 24 or 48 hours at 18 to 20° C., and that there is, on the contrary, a tendency for it to diminish in numbers while the saprophytic bacteria multiply rapidly. The size of the inoculation is shown to be without effect. If a cow's udder is once infected it can excrete thousands of haemolytic streptococci per ml., and may continue to do so for weeks, or even months. It is contended, in view of these findings, that though the ultimate source of infection is probably a human carrier, the spread of streptococcal infections, such as tonsilitis and scarlet fever, cannot be attributed to any material extent to droplet infection from milkers and other people handling the milk, and that the major part of the spread of such infection must be played by infected cows. It is urged that investigation of apparent milk-borne epidemics should include immediate bacteriological examination of the milk of every individual cow contributing to the supply. D. R. W.

Epidemic of Paratyphoid B. Fever in Liverpool and District. W. M. Frazer, B. T. J. Glover and V. Glass. (*Brit. Med. J.*, August 21st, 1937.)—The outbreak occurred early in January, 1937, and aggregated 132 primary cases before it was ended. The history given by the majority of patients showed that they obtained their milk or butter or bread from the same firm referred to as firm A. Firm A traded through many retail shops over an area corresponding with that covered by the outbreak. As a number of the patients had obtained their butter from some other source, this article was soon eliminated from those suspected. The milk was all pasteurised and sterilised, the pasteurising plant being one of the latest design and the bottling apparatus such that the milk is not touched by hand after pasteurisation. Moreover, the milk supplied by firm A is approximately one-fifth the daily consumption for Liverpool, so that the outbreak would have been much greater had it been due to the infection of this milk. The bakery is a very large one and very well-conducted. Out of 123 patients, 76 (62 per cent.) regularly consumed bread from this source. Examination of the blood of the 20 employees in this bakery showed that the blood of one gave positive agglutination with *B. paratyphosum* B. (H) in dilution 1 in 20, and subsequent examination of the stools and urine of this employee, showed the presence of *B. paratyphosum* B. on many occasions from the 9th February to the 8th March. The organisms isolated were typed according to the five types of Kristensen and Bojlén depending upon the rate of fermentation of rhamnose, fermentation of inosite and behaviour in the Bitter test (1926). Ninety-five strains from 48 cases (including the carrier) were tested and all fell into the same group R_3I_1. Experiments were conducted to see if paratyphoid B. could be recovered from crusts of bread smeared with a saline suspension of these organisms. It was shown that when 120 were added, some could be recovered on the 6th day, but not on the 7th day after inoculation, the crusts being stored in the meantime at room temperature in a dark cupboard. With an inoculum of 4 million organisms, they were recovered on the 22nd day but not on the 23rd. One striking feature of the investigation was the large percentage of instances in which *B. paratyphosum* B. was recovered from the stool, *viz.* 83 per cent. in the first week of illness, thereby facilitating early diagnosis, and 92, 92, 87·5, 100, 75, and 77·7 per cent. in the 2nd, 3rd, 4th, 5th, 6th, and 7th weeks, respectively. (These results were obtained by the use of E. R. Jones's brilliant green—eosin medium, ANALYST, 1937, 817.)

D. R. W.

Autolytic System of Pneumococci. R. J. Dubos. (*J. Exper. Med.*, 1937, V, 65, 873–83; *Bull. Hyg.*, 1937, 12, 728.)—A bacteriolytic enzyme is present in all pneumococci and is liberated by the autolysis of this organism. A crude preparation of the enzyme was prepared by allowing a thick suspension of young pneumococci in saline to autolyse in the presence of toluene for 24 hours at 37° C. The product is active in high dilution; a strong dose will "lyse" rough and smooth types of heat-killed pneumococci, and a small dose will render them Gram-negative without lysis. Attempts were made to purify the preparation by centrifuging an acidified suspension, re-suspending the deposit in buffered solution and, after sedimentation, filtering through a Berkfeld V. candle. The enzyme acts best over a *p*H range of 8 to 5·5; it is heat labile and inactivated by papain, trypsin, bile and oxidising agents. Organisms subjected to the action of trypsin were rendered Gram-negative but not dissolved by the enzyme. Incubation of the enzyme with certain amino-polysaccharides was found to remove its power of altering pneumococci, suggesting that this enzyme and one that is known to hydrolyse these polysaccharides are the same. D. R. W.

Toxicological and Forensic

Rapid Method for Isolation of Organic Poisons. C. P. Stewart, S. K. Chatterji and S. Smith. (*Brit. Med. J.*, 1937, 790–792.)—It has been found that in the extraction of alkaloidal poisons from viscera the lengthy Stas–Otto method may be replaced by treatment of the minced material with 10 per cent. trichloroacetic acid. This at once yielded a water-clear filtrate which was free from protein and fat and which contained the whole of the alkaloid originally present. From the solution the alkaloid was removed by adsorption on kaolin, from which it was eluted by hot chloroform. After removal of the alkaloids veronal was adsorbed on charcoal and eluted with ether. The method is being investigated further and extended to other organic poisons. S. G. S.

Detection of Traces of Metals Deposited by Small-Arm Fire. A. Brüning and M. Schnetka. (*Chem.-Ztg.*, 1937, 61, 827–828.)—A bullet-wound produced at close range (up to about 25 cm.) shows a smoky patch around the point of entry of the bullet consisting of propellant residues and traces of metallic fouling produced during the passage of the bullet along the barrel. The following methods are proposed for detecting lead, copper, nickel and zinc in the smoky patch formed on fabric. The affected patch (about 2 to 3 sq. cm.) is cut out and digested in about 3 ml. of warm nitric acid (sp.gr. 1·14). The acid is then poured off, the fabric is washed with a little water, and the combined liquids are filtered and evaporated to dryness on the water-bath. The residue is dissolved in 1 to 2 ml. of water, and the solution is neutralised with ammonia. *Lead.*—The diphenyl thiocarbazone test is used: 0·2 ml. of a diphenylthiocarbazone solution in carbon tetrachloride (10 mg. in 100 ml.) and 0·2 ml. of 5 per cent. potassium cyanide solution are placed in a small test-tube, a drop of the test solution is added, and the whole well shaken. The presence of lead is shown by the development of a red colour. It is pointed out that the only other metal likely to give a red colour in the test is bismuth, which is ordinarily absent from small-arms ammunition. *Copper.*—The rubeanic acid reaction is used. A few drops of a 0·5 per cent. alcoholic solution of rubeanic acid are placed on a piece of filter-paper and dried. A drop of the test solution is added to the reagent-spot, and the paper is held over the mouth of an ammonia-bottle. If copper is present a black spot or ring is formed, which, on the addition of a drop of yellow ammonium sulphide, disappears more or less completely (sensitiveness, 0·006γ). Any undissolved black material indicates the presence of iron. The presence in the black precipitate, of violet particles not dissolved by ammonium sulphide, indicates nickel. Lead and zinc do not interfere. As an alternative method for detecting copper, Ritter's test may be used, in which a blue colour is produced with traces of copper by the addition of dimethyl-*p*-phenylenediamine, α-naphthol, hydrogen peroxide and sodium hydroxide. *Nickel.*—Dimethylglyoxime is used in the ordinary way as a spot reagent on filter-paper. *Zinc.*—Traces of zinc give a red colour with diphenylthiocarbazone; nickel, copper and lead also give colours with the reagent, but these colours can be suppressed by the addition of a polysulphide, permitting the detection of 0·2γ of zinc in the presence of 10γ of nickel, copper and lead, as follows:—In a 10-ml. tube 1 ml. of diphenylthiocarbazone solution in carbon tetrachloride (10 mg. in 100 ml.) is well mixed with 5 to 6 ml. of water, giving a green colour; 0·2 ml. of sodium disulphide solution (7·5 g. of pure sodium sulphide crystals are dissolved in 10 ml. of water; 1 g. of sulphur is dissolved in the solution by warming, and the solution is diluted to 75 ml.) is added and mixed by shaking. The solution should now be practically colourless. A few drops of the test solution are added and the liquid is shaken; a strong red colour is produced if a few thousandths of a mg. of zinc are present. The use of the purest distilled water is necessary in these tests, owing to their high sensitivity.

S. G. C.

Agricultural

Determination of Ferrous Iron in Soil Solutions by means of 2 : 2′-Dipyridyl. V. Ignatieff. (*J. Soc. Chem. Ind.*, 1937, 56, 407–410T.)—In the range of *p*H from 3·5 to 8·5, 2 : 2′-dipyridyl forms with ferrous iron, stable complex compounds which have a deep red colour and are strongly resistant to atmospheric oxidation. The reagent consists of 0·0625 g. of 2 : 2′-dipyridyl and 0·8 ml. of *N*-hydrochloric acid dissolved in water and diluted to 25 ml.; 1 ml. of the solution contains an amount of dipyridyl in excess of that required to react with 140×10^{-6} g. of ferrous iron. One ml., or more, of the reagent is added to 10 ml. of acetate buffer solution of *p*H 4·6 contained in a Nessler glass; 5 to 10 ml. of the clear and colourless soil solution are added, and the liquid is diluted to 25 ml. The red colour, which develops immediately, is matched against a standard prepared by adding sufficient *M*/400 ferrous ammonium sulphate solution to the same amount of reagents and buffer solution contained in another Nessler glass, and diluting to 25 ml. Coloured and turbid soil solution may be decolorised and clarified by adding 2 per cent. of aluminium chloride and some mineral oil and centrifuging. Alternatively, a 2 per cent. solution of aluminium chloride may be advantageously used, instead of distilled water, for extracting the soil samples. Aluminium chloride appears to restrain the atmospheric oxidation of ferrous iron in aqueous solution. Ferric iron in solution is slowly reduced by dipyridyl in presence of light; no error from this cause, however, is likely if the colorimetric comparison is completed within an hour or two. S. G. C.

Organic

Two New Colour Indicators derived from β-Naphthylamine. H. Eichler. (*Chem.-Ztg.*, 1937, 61, 797–798.)—"β-Naphthylamine red" (β-naphthylamine-α-E-anthranilic acid) is prepared by coupling equivalent quantities of β-naphthylamine and diazotised anthranilic acid dissolved in water containing 1 g. mol. of hydrochloric acid for every g. mol. of the reaction product. It may be crystallised from ethyl alcohol or methyl alcohol, and a solution of the free acid in either of these solvents is yellow in alkaline solution and red in the presence of acid; the red colour flocculates after a short time. The sodium or potassium salts are obtained by neutralisation with an equivalent quantity of the appropriate alkali hydroxide or carbonate, and salting-out, and the ammonium salt results on evaporating a solution of the acid in dilute ammonia. These salts are readily soluble and are recommended for use as indicators. "β-Naphthylamine orange" (β-naphthylamine-α-E-sulphanilic acid) is prepared from diazotised sulphanilic acid by a similar method, and has similar properties. It is orange-red in the presence of acids, and yellow-orange in alkaline solution. Both end-point changes are sharp, so that the indicators can replace methyl orange or methyl red. Analogous azo-compounds (*e.g.* prepared from diazotised aniline or *o*-anisidine) are very soluble, but do not give good end-point colour changes. The ammonium salts of methyl orange, Congo red and methyl red are more soluble in water than the sodium salts, and may conveniently replace these. They are prepared by precipitating the dyestuff with acid, and evaporating to dryness a solution of the precipitate in ammonia. It is suggested that the adjective "readily soluble" should be added to the name of the indicator in order to designate a salt which is more soluble than the dyestuff from which it is derived. Solutions of *H*-acid in water or of β-naphthol in alcohol serve as fluorescence indicators, and have a blue fluorescence in neutral or alkaline solutions, which disappears on acidification. J. G.

Identification of Alkyl Halides, Amines and Acids. E. L. Brown and N. Campbell. (*J. Chem. Soc.*, 1937, 1699–1701.)—Thiourea is a suitable reagent for the identification of the alkyl bromides and iodides. S-alkylthioureas are formed and these yield picrates with sharp melting-points and characteristic crystalline structure. The method is not generally applicable to alkyl chlorides, although it serves to identify benzyl chloride. Phenyl thiourea, since it reacts only with straight-chain compounds, is a less satisfactory reagent. Finely-powdered thiourea (0·2 g.) and an equal amount of the alkyl bromide or iodide are heated with 2 ml. of alcohol for 2 minutes. Picric acid (0·2 g.) dissolved in the minimum amount of boiling alcohol is added, and the picrate which separates on cooling is recrystallised from alcohol until its m.p. is constant. Phenyl isothiocyanate, frequently used in the identification of amines, is a somewhat unsatisfactory reagent; among the other isothiocyanates which were tried, 4-diphenylyl isothiocyanate and β-naphthyl isothiocyanate gave good results. The thiocarbanilides necessary for the preparation of the isothiocyanates were prepared by Fry's method (*J. Amer. Chem. Soc.*, 1913, **35**, 1544), and the isothiocyanates by Steudemann's method (*Ber.*, 1883, **16**, 549). 4-Diphenylyl isothiocyanate forms light brown needles on recrystallising from glacial acetic acid and, on recrystallising from alcohol, is obtained as colourless needles, m.p. 70° C. The amine (0·2 g.) and the isothiocyanate (0·2 g.) are heated together for about 20 seconds, and 2 ml. of 50 per cent. alcohol are added. The thiourea deposited on cooling is recrystallised from 50 per cent. alcohol. 2 : 4 : 5-Trinitrotoluene, used by Barger and Tutton (*Biochem. J.*, 1918, **12**, 402) to identify amino-acids, the 5-nitro-group being replaced, was found to be a good reagent for the identification of small amounts of certain amines, a 10 per cent. alcoholic solution yielding instantly a clean precipitate of the substituted alkyl aniline. It reacts only with primary amines and, with the higher amines, gives oily products. The reagent (0·1 g.) is dissolved in 1 ml. of alcohol, and 3 or 4 drops of the amine are added. The 4 : 6-dinitro-*N*-alkyl-*m*-toluidine separates immediately, and yields yellow or orange needles after recrystallisation from alcohol. Monobasic aliphatic acids react with *o*-phenylene-diamine to form 2-substituted benziminazoles which have been used for the identification of the acids (Seka and Müller, *Monatsh.*, 1931, **57**, 97). For melting-point determinations the picrates of the 2-alkyl-benziminazoles are more convenient. The method recommended for their preparation is that of Phillips (*J. Chem. Soc.*, 1928, 2393). A mixture of 0·5 g. of *o*-phenylene-diamine, 0·5 to 1 g. of the organic acid and 4 ml. of *N* hydrochloric acid is heated beneath a reflux condenser for 15 minutes, cooled and treated with aqueous ammonia solution until the benziminazole separates. This is washed with water, dissolved in the minimum amount of boiling alcohol and added to a solution of 0·5 g. of picric acid in the minimum amount of boiling alcohol. The precipitate which separates on cooling is recrystallised from alcohol. A 1 per cent. alcoholic solution of 2-phenylindole may be used for the detection of small amounts of alkyl nitrite, the compound formed being 3-oximino-2-phenylindole. 2-Phenylindole (0·1 g.) is dissolved in boiling alcohol, and 0·1 g. of the alkyl nitrite is added. The oximino-compound separates on cooling and is recrystallised from amyl acetate in orange, diamond-shaped needles, m.p. 280° C. (decomp.). Amines may be identified as 2 : 4-dinitrobenzoates (Buehler and Calfee, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 351; Abst., ANALYST, 1934, **59**, 769). The following is an improved method of preparing 2 : 4-dinitrobenzoic acid:—Fuming nitric acid (500 ml.) is added slowly, with cooling, to phenyl-acetic acid (50 g.), and the mixture is heated beneath a reflux condenser for 1 hour and then poured into water. The precipitate is washed with cold water and recrystallised from water (4 parts) and alcohol (1 part). Its m.p. is 181 to 182° C., and the yield is about 45 g. The melting-points of the condensation products of a number of halides, amines and acids with the reagents described are given. A. O. J.

Determination of Nitrogen in Betaine, Pyramidone and Sulphanilic Acid by Hydrogenation. H. ter Meulen and H. J. Ravenswaay. (*Rec. Trav. Chim. Pays-Bas*, 1937, **56**, 1022–1023.)—In comparing the results of the determination of nitrogen by different methods, Gauduchon (*Contribution a l'Étude de la*

Méthode de Kjeldahl. Emploi de l'Acide Perchlorique. Paris, 1936) found that the hydrogenation method gave good results except with betaine hydrochloride (8·47, against the theoretical value of 9·11 per cent.), pyramidone (16·88, against 18·19), and sulphanilic acid (5·46, against 8·09). With carefully purified samples the hydrogenation process gave the following results, which accord well with theory: betaine hydrochloride, 9·07 to 9·10; pyramidone, 18·05 to 18·15; sulphanilic acid, 8·00 and 8·03 per cent. Too rapid heating is a frequent source of error but, since Gauduchon found a low figure (8·27 per cent.) for nitrogen in betaine hydrochloride by the Kjeldahl process (Lauro technique), it must be concluded that her sample was impure, especially as the authors obtained 9·00 to 9·02 per cent. with pure samples. Gauduchon used pure nickel as catalyst; it has been shown (ter Meulen, *Rec. Trav. Chim. Pay-Bas*, 1934, **53**, 118) that nickel containing 10 per cent. of thorium oxide is a more efficient catalyst. In applying the hydrogenation process to compounds containing a halogen element, it is advisable to introduce a little soda-lime into the quartz tube containing the catalyst (ter Meulen and Ravenswaay, *Chem. Weekblad*, 1936, **33**, 248) in order to prevent de-sensitisation of the catalyst by the halogen element (*cf.* Abst. and Note, ANALYST, 1932, **57**, 524).

A. O. J.

Composition of some less common Vegetable Fibres. A. G. Norman. (*Biochem. J.*, 1937, **31**, 1575–1578.)—The composition of twenty-seven fibres, mostly of tropical origin, is reported. Nigerian jute was found to be almost identical with Indian jute, except for a lower xylan content, and Bimlipatam jute (*Hibiscus cannabinus*) contained only half as much lignin as true jute. A sample of *Urena lobata* grown in Uganda differed considerably in composition from a sample of the same species grown in India, but *Sida rhombifolia* from India and Sierra Leone were very similar. Palmyra fibre resembled coir, and sunn hemp from India was similar to European hemp. Bowstring hemp (*Sansevieria guineensis*) and Mauritius hemp (*Furcraea gigantea*) are not true hemps; they had high xylan-contents. Baobab fibre contained less cellulose than many of the other fibres, but its lignin-content was not high, and the xylan fraction of the cellulose was not as high as in most wood celluloses. Pita fibre from Colombia differed considerably from previously reported "Pita grass," but there appears to be some confusion in the description of this fibre. Tucum fibre or Tucum palm fibre from the Amazon valley and Brazilian coasts had a high cellulose-content, but the furfural yield and the xylan in the cellulose were low. This is the only leaf fibre in the low xylan group. Kapok from the seed bolls of *Eriodendron anfractuosum* was very different from cotton. The cellulose-content was only 65 per cent., and this contained a large amount of xylan. S. G. S.

Determination of Lignin. Acid Pre-treatment and the Effect of the Presence of Nitrogenous Substances. A. G. Norman. (*Biochem. J.*, 1937, **31**, 1567–1574.)—In the determination of lignin in plant materials interference may be caused by the condensation of aldehydes or phenolic substances with the lignin. The observation that after intermittent acid hydrolysis slightly lower yields of lignin are obtained than after continuous hydrolysis, has been confirmed. This may be due either to the formation of some non-lignin insoluble product or to the condensation of some soluble product with the lignin. The acid pre-treatment in the lignin determination is not rejected, although its suitability is doubted. The increased yields of apparent lignin in the presence of protein are probably due to the condensation of large, partially deaminated protein fragments. Simple amino acids and nitrogenous bases have a much smaller effect. S. G. S.

Isolation of Pectic Substances from Wood. E. Anderson, L. W. Seigle, P. W. Krznarich, L. Richards, and W. W. Marteny. (*J. Biol. Chem.*, 1937, **121**, 165–174.)—Extraction of mature wood with dilute solutions of sodium hydroxide, hydrochloric acid and ammonium hydroxide removed a part only of the hemicelluloses and pectic materials. If the wood was then treated with chlorine gas and afterwards with alcohol, the remainder of the pectic material and hemicelluloses was extracted with the proper solvents. The method described by Anderson (*J. Biol. Chem.*, 1935, **112**, 531) was used for preparing the wood and dissolving the hemicelluloses and pectic material, but the procedure for precipitating the pectic material was modified. Both pectin A (the 0·05 *N* hydrochloric acid extract) and pectin B (the 5 per cent. ammonium hydroxide extract) were acidified with hydrochloric acid to give an acidity of 0·1 *N* and the pectic matter was precipitated by the addition of 4 volumes of ethanol. After the precipitate had settled, the liquid was siphoned off, and the precipitate was removed by centrifuging. After the more soluble portions of the hemicelluloses and pectic materials had been extracted, the remaining pulp was washed with water and very dilute hydrochloric acid. It was then mixed with water and shaken mechanically while chlorine gas was passed into the solution for four hours. The coloured solution was filtered from the pulp, and the latter was washed with water. It was then extracted for 2 hours with boiling ethanol beneath a reflux condenser. The pulp was filtered off, washed thoroughly with warm ethanol, shaken with 8 per cent. ammonium hydroxide for 48 hours, and filtered. The filtrate was acidified with hydrochloric acid and pectin C was precipitated by the addition of 4 volumes of ethanol. To remove the hemicelluloses made soluble by chlorination, the pulp was extracted twice with 5 per cent. sodium hydroxide solution, each time for 48 hours. The filtrates were acidified with hydrochloric acid and separated into a water-insoluble portion, hemicellulose C, and a water-soluble portion, hemicellulose D. The latter was precipitated by addition of ethanol. The method used for the purification of the pectin depended on the form in which it was present as well as on the impurities present. When the material was present as pectic acid, it was dissolved in 40 times its weight of 5 per cent. ammonium hydroxide and filtered from impurities, and the filtrate was acidified with hydrochloric acid. If the resulting precipitate of pectic acid was coloured, chlorine gas was passed into the acid solution for a short time and ethanol was added. When the impure material was present as the dry calcium or barium pectate it was purified by shaking with 100 times its weight of 1 per cent. hydrochloric acid, and separating the pectic acid by centrifuging, dissolving it in ammonium hydroxide and treating it as previously described. When starch was present it was either removed by treatment with diastase or the pectin was converted into the insoluble calcium salt as described by Branfoot (*The Pectic*

Substances of Plants, London, 1929). Uronic acid was determined by the method of Lefèvre and Tollens with the apparatus described by Dickson, Otterson and Link (*J. Amer. Chem. Soc.*, 1930, 52, 775). Pentosan was determined by distillation with 12 per cent. hydrochloric acid and precipitation of the furfural with phloroglucinol. Specific rotations were determined by dissolving the pectic acid in 2 per cent. ammonium hydroxide solution. The presence of galacturonic acid was established by the method of Heidelberger and Goebel (*J. Biol. Chem.*, 1927, 74, 613). When the amount of furfural obtained was over 23 per cent., the amount of carbon dioxide was below 16·5 per cent. and the optical rotation was below +200°, hemicelluloses were present. S. G. S.

Inorganic

Determination of Mercury and Mercurous Chloride in Ores. J. J. Fahey. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 477–478.)—The weighed sample, ground to pass a 60-mesh screen, is introduced into a Pyrex tube (length 50 cm., internal diameter 0·8 cm.), open at both ends, which is placed in an electric furnace, dry air being passed through the tube during heating. A layer of dry granulated sodium carbonate, 2·5 cm. long, is placed near the ore, with an asbestos plug between the two. A tightly rolled gold sheet fitting tightly into the tube is inserted into its cold exit end outside the furnace. The temperature is raised to 650° C, and kept at that point for 5 minutes while the air passes at the rate of 4 to 6 bubbles per second. The mercury and calomel volatilise, and the latter, passing over the sodium carbonate, is decomposed, with formation of sodium chloride. The mercury condenses in the cold part of the tube and is made to pass through the gold coil by means of gentle heating with a Bunsen burner. When the tube is cold, the gold coil is withdrawn and weighed, then heated (at first gently, then with the full flame of a Bunsen burner), and again weighed. The difference between the two weights gives the total mercury-content of the ore. For the determination of the mercury present as chloride, the glass tube is broken at the point where the asbestos plug separates the ore from the sodium salt. The latter is transferred to a beaker and dissolved in water, and the solution is acidified with nitric acid and filtered to remove any asbestos fibres. The filtrate is treated in the usual manner with silver nitrate solution for the gravimetric or nephelometric determination of the chlorine, which is calculated to HgCl. The method is stated to give very good results with quantities of mercurous chloride not exceeding 0·05 g.; alkali chloride does not interfere. W. R. S.

Iodimetric Determination of Tin. M. Hegedüs. (*Z. anal. Chem.*, 1937, 110, 338–348.)—In order to avoid the negative error in the titration of stannous chloride with iodine, due to oxidation of the tin by oxygen dissolved in the standard iodine solution, the author proposes adding a known excess of very strong iodine solution (freshly prepared from excess of potassium iodide and an accurately known amount of potassium bromate) to the reduced air-free tin solution in an atmosphere of carbon dioxide, and titrating the excess iodine with thiosulphate. For a description of the reduction flask and the somewhat involved working directions, reference should be made to the original paper. W. R. S.

Gravimetric Determination of Cobalt as Dipotassium Sodium Cobaltinitrite. C. F. Cumbers and J. B. M. Coppock. (*J. Soc. Chem. Ind.*, 1937, **56**, 405T–407T.)—The degree of hydration and conditions of formation of dipotassium sodium cobaltinitrite have been studied, the temperature of precipitation being varied from 20° to 100° C. The composition of the precipitate was that of the monohydrate only at a precipitation temperature of 60° C.; at lower temperatures the degree of hydration was greater, and *vice-versa.* Particle size increased with increasing temperature, reaching a maximum at 60° C. Precipitates of the theoretical composition of the monohydrate were obtained when the Na:K ratio in the liquid ranged from 15:1 to 40:1 (at 60° C.); outside this range variations in composition occurred. The monohydrate remained stable on heating at 150° C. The following method was adopted for gravimetric determination of cobalt:—The cobalt solution (10 to 25 ml.), acidified with 0·5 to 1 ml. of glacial acetic acid, was heated to 60 ± 2° C. The reagent (30 g. of sodium nitrite and 1·25 g. of potassium chloride dissolved in 35 ml. of hot water; 1 ml. of this solution is required for each 6·5 mg. of cobalt), heated to 70° C., was slowly added from a pipette, with stirring. After 15 minutes' heating the liquid was allowed to cool for half-an-hour; the precipitate was filtered off on a sintered glass filter, washed with a saturated solution of the precipitate and dried at 120° to 130° C. Alternatively, the precipitate was washed successively with alcohol and dry ether, dried in a vacuum desiccator for 10 minutes, and weighed. The precipitate had the composition $K_2NaCo(NO_2)_6,H_2O$. Good results were obtained with about 65 mg. of cobalt taken. The results of tests of the precipitation of the complex in the presence of nickel indicated some tendency for co-precipitation to occur. Ammonium salts in small amounts, *e.g.* 100 mg. of ammonium sulphate, did not interfere, for although ammonium cobaltinitrite is stable at 20° C. and is insoluble, it is decomposed at 60° C. Tests of the applicability of the cobaltinitrite method to the determination of potassium indicated that the Na:K ratio for precipitation of dipotassium sodium cobaltinitrite monohydrate was more restricted in range than for the determination of cobalt, the results as a whole showing the necessity for using a standard potassium solution of approximately the same concentration as those being examined in order to obtain the "potassium factor."

S. G. C.

Gravimetric Determination of Chromic Acid as Lead Chromate. D. Tschawdarov and N. Tschawdarowa. (*Z. anal. Chem.*, 1937, **110**, 348–354.)—The authors secured accurate results by using lead nitrate (not acetate) as precipitant in a dilute nitric acid solution. The liquid to be tested is acidified with 10 to 15 ml. of 2 *N* nitric acid per 200 ml., heated to boiling, and precipitated, drop by drop, during continuous stirring, with 3 to 5 g. of lead nitrate dissolved in 30 ml. of water. After standing for 6 to 12 hours the liquid is filtered through a porous glass crucible (Jena I.G.3); the precipitate is washed several times with cold, and finally with hot water, and heated at 160° to 180° C. to constant weight. Chloride should not be present; acetate causes formation of a finely-divided precipitate, but free acetic acid is harmless. The process can be applied to solutions containing alkalis, alkaline earths, iron, aluminium, cadmium, copper, manganese and zinc.

W. R. S.

Gravimetric Determination of Zirconium by Means of Methylarsinic Acid. R. Chandelle. (*Bull. Soc. Chim. Belg.*, 1937, **46**, 283–300.)—Disodium methylarsinate precipitates zirconium from acid solution as white, flocculent $Zr(CH_3AsO_3)_2$. The cold, 0·2 *N* acid chloride solution is treated with an excess of the solid reagent, heated to boiling, and boiled for a few minutes until the precipitate flocculates. After settling for some hours, or preferably overnight, it is collected, washed with 0·2 *N* hydrochloric acid and finally with water. Filter and precipitate are dried in a tared crucible, charred at low temperature, ignited until the precipitate is quite white, and weighed. This weight is excessive, owing to incomplete elimination of the arsenic. A known weight of the precipitate is therefore transferred to a tared porcelain boat, which is ignited in a silica tube in a current of hydrogen. After cooling, the boat is withdrawn and heated in the air, when the slightly discoloured precipitate turns white. When cold, it is weighed as ZrO_2. The procedure separates zirconium from aluminium, chromium, nickel, cobalt, zinc, manganese, calcium and magnesium, but iron interferes. The author applies extraction with ether to remove iron from the solution prior to precipitation of zirconium as described above. Precipitation from sulphuric acid solution is not recommended, as the recovery is less complete. W. R. S.

Determination of Magnesium in Aluminium Alloys. I. Ubaldini and U. Pelagatti. (*Chim. e Ind.*, 1937, **19**, 131–133.)—The following methods are recommended. (1) *Alloys containing no Manganese.*—Two g. of the sample are treated with 20 to 25 ml. of a 25 per cent. solution of sodium hydroxide in a 500-ml. flask covered with a small funnel. The reaction is begun at room temperature and continued on the water-bath when the vigorous evolution of hydrogen ceases. When practically all the alloy has dissolved, the liquid is diluted with 250 ml. of hot water and filtered, and the residue of magnesium hydroxide and unattacked metal is washed with hot 1 per cent. sodium carbonate solution. The filter-paper is transferred to a flask and heated on the water-bath with 15 ml. of dilute (1:1) nitric acid until no further fumes are evolved, after which the liquid is diluted with hot water and filtered, and the residue is washed with water containing a few drops of nitric acid. After cooling, the filtrate is neutralised with ammonia and treated with 10 ml. of ammonium citrate solution (prepared by neutralising 400 g. of crystallised citric acid with ammonia of sp.gr. 0·92 and making up to 1 litre with water), followed by 40 ml. of conc. ammonia and 30 ml. of 10 per cent. sodium phosphate solution. The precipitated magnesium ammonium phosphate is determined as pyrophosphate by the usual method. When the alloy contains more than 1 per cent. of silicon the procedure is modified by evaporating the nitric acid solution of the metals on the water-bath with sulphuric acid until white fumes are evolved, cooling, taking up with water, filtering off the silica, and precipitating the magnesium as described above.

(2) *Alloys containing Manganese.*—The procedure is as described up to the stage of treatment with nitric acid and the elimination of the silica, if necessary. The acid solution of the metals, which should have a volume of about 300 ml., is neutralised with ammonia, treated with 3 to 4 ml. of conc. nitric acid and 2 g. of ammonium persulphate, and boiled until all the manganese has been precipitated

(silver, which catalyses the oxidation to the stage of permanganic acid, must not be present); 10 minutes' boiling is generally more than sufficient. The precipitate is filtered off and washed with 2 per cent. nitric acid, ammonium citrate is added to the filtrate, and the magnesium is precipitated as described above.

Tables I and II show results thus obtained.

TABLE I

DETERMINATION OF MAGNESIUM IN SOME COMMERCIAL ALLOYS

	Mg. ppt'd. after double ppt'n. of			
Sample No.	Group IV with NH_4OH and NH_4Cl in presence of H_2O_2 Mg. found, per cent.	Groups III and IV with $(NH_4)_2S$ Mg. found, per cent.	Mg. ppt'd. directly in presence of ammonium citrate Mg. found, per cent.	Remarks
1	1·16	—	1·58	Alloy containing aluminium, copper, magnesium, manganese, iron, silicon.
2	1·26	—	1·50	
3	1·58	—	1·68	
4	1·25	—	1·55	
5	—	1·56	2·14	Alloy containing aluminium, copper, magnesium, nickel, iron, silicon.
6	—	1·85	2·15	
7	—	2·05	2·05	
8	—	1·79	2·10	

TABLE II

DETERMINATION OF MAGNESIUM IN CONTROL SOLUTIONS CONTAINING KNOWN QUANTITIES OF MAGNESIUM

	Mg. ppt'd after double ppt'n. of				
Test No.	Group III with NH_4OH and NH_4Cl in presence of H_2O_2 g.	Groups III and IV with $(NH_4)_2S$ g.	Mg. ppt'd. directly in presence of ammonium citrate g.	Mg. present g.	Difference g.
1	0·0184	—	—	0·0330	−0·0146
2	0·0230	—	—	0·0330	−0·0100
3	—	0·0378	—	0·0460	−0·0082
4	—	0·0404	—	0·0460	−0·0054
5	—	—	0·0325	0·0330	−0·0005
6	—	—	0·0452	0·0460	−0·0008

The solutions used for the determinations in Table II contained (in addition to magnesium) copper, iron, manganese, and nickel in quantities corresponding with those found in commercial alloys. E. M. P.

New Procedure for the Determination of Fluorine by the Peroxidised Titanium Method. D. Dahle. (*J. Assoc. Off. Agr. Chem.*, **1937, 20,** 505–516.)—Determination of fluorine by the peroxidised titanium method is subject to certain possible sources of error, such as impurities derived from filter paper, abnormal behaviour of the distillate obtained by Willard and Winter's method (*Ind. Eng.*

Chem., Anal. Ed., **1933**, **5**, 7; Abst., ANALYST, **1933**, **58**, **242**) when the amount of fluorine present is small, and inequalities in the *p*H of standard solution and sample. Dahle and Wichmann (*J. Assoc. Off. Agr. Chem.*, **1936**, **19**, **320**; **1933**, **16**, **612**; Abst., ANALYST, **1934**, **59**, **132**) showed that the addition of aluminium salts to a peroxidised titanium solution has no effect upon the colour, but largely counteracts the bleaching of the colour by fluorine. If the same amount of peroxidised titanium solution is added to two equal aliquot portions of a sample distillate to one of which an aluminium salt has been added, the colour difference between the two portions should be a measure of the fluorine present irrespective of any inherent colour in the original solution, provided that the addition of aluminium salt causes no change in the *p*H value. Experiments were carried out with the neutral wedge photometer of Clifford (*J. Assoc. Off. Agr. Chem.*, **1936**, **19**, **130**), fitted with a Corning No. 511 violet filter and a Noviol Shade No. 038, which proved that 0·7 mg. of titanium oxide per 50 ml. gives a satisfactory colour, and that the bleaching caused by amounts of fluorine of the order of 0·1 mg. is the same for any *p*H value within the limits 1·1 and 1·5, the unbleached comparison solution having the same *p*H. Further experiments showed that for quantities of less than 0·1 mg. of fluorine, 10 mg. of aluminium in the form of a salt counteracts the bleaching effect, and that although the depth of colour of peroxidised titanium solutions, with or without fluorine, decreases with the temperature, the effect is negligible for differences of 1 to 2° C. The formation of the aluminium-fluorine complex is instantaneous at 27° C. in the absence of titanium ions, but is affected both by the temperature and by the presence of titanium ions. The solutions required for the determination are as follows:—Aluminium nitrate solution: 140 g. of $Al(NO_3)_3.9H_2O$ in 1 litre of water, 1 ml. containing 10 mg. of Al; sodium fluoride solution: a stock solution of 2·2 g. per litre diluted fifty-fold as required, 1 ml. containing 0·02 mg. of fluorine; titanium chloride solution prepared by diluting a suitable amount of conc. titanium chloride solution with 200 ml. of dilute nitric acid (1 + 9) and water to 1 litre, so that 1 ml. contains 0·35 mg. of TiO_2; a 6 per cent. solution of hydrogen peroxide. For *p*H adjustment a block comparator is used with *m*-cresol purple or acid cresol red or any indicator covering the *p*H range 1·1 to 1·5. The determination is effected by means of four solutions. The "standard zero" solution is made by mixing 2 ml. of titanium solution, 2 ml. of peroxide and 2 ml. of dilute nitric acid (1 + 9), and diluting to exactly 50 ml.. The "standard fluoride" solution is made in the same way, but includes 2·5 ml. of the sodium fluoride solution. The "sample *x*" is an aliquot portion of the distillate containing 0·05 mg. (±0·005 mg.) of fluorine if possible, or less if necessary, to which are added 2 ml. of the standard titanium solution, 2 ml. of hydrogen peroxide solution, 2 ml. of dilute nitric acid and water to exactly 50 ml. The "sample zero" is prepared in the same manner as "sample *x*" from an equal aliquot portion of the distillate, with the difference that 1 ml. of the aluminium nitrate solution is added and the mixture is inverted at least seven times before the other reagents are added. Verification that the *p*H value lies within the range should be made for one standard and one sample solution. Ten to 15 photometer readings should be taken for each solution, and it may be necessary to discard the first few readings, which are often high owing to slow eye adjustment. The eyes should be rested frequently by looking at a yellow or light tan surface. From the average of the readings the mg. (F) of fluorine in the sample solution is calculated by means of the formula

$$\frac{\text{Sample zero—Sample } x}{\text{Standard zero—Standard 0·05F}} = \frac{\text{F}}{0·05}$$

Four-inch glass cells of capacity 15 to 25 ml. are recommended. The method is directly applicable to the determination of fluoride in the presence of relatively large amounts of chloride (*e.g.* in sea water). As a rapid qualitative test for fluorides in water supplies the process can be carried out in Nessler glasses and, with the aid of the photometer, it can subsequently be made quantitative. The interference of a number of common acidic and basic ions was investigated. With the exception of iron and aluminium ions, the ions which often interfere in the micro-determination of fluorine do not cause any errors. A. O. J.

Microchemical

References of Microchemical Interest. P. Haas. (*Mikrochimica Acta*, 1937, 1, 300–312.)—References to the current journals, with titles of the papers, are arranged alphabetically according to the authors under the following headings:—I, Inorganic Chemistry (preparative and analytical); II, Physico-chemical and Physical Methods; III, Organic Chemistry (preparative and analytical); IV, Biochemical (animal and human); V, Medico-chemical Methods; VI, Pharmacy, Toxicology, Forensic Chemistry, and Allied Subjects; VII, Plant Physiology, Agricultural Chemistry, Chemistry of Foodstuffs; VIII, Applied Chemistry (technical chemistry, mineralogical chemistry, etc.); IX, Apparatus. J. W. M.

References of Microchemical Interest. P. Haas. (*Mikrochimica Acta*, 1937, 1, 366–378.)—Further references to current journals arranged under the same headings as described in the preceding abstract. J. W. M.

Micro-volumetric Determination of Nitrate Nitrogen. L. Szebellédy and M. Ajtai. (*Mikrochimica Acta*, 1937, 1, 255–259.)—The well-known method of titrating nitrates with 0·1 *N* ferrous sulphate solution in a strongly acid solution has several disadvantages which may be overcome by substituting *N*-ferrous sulphate solution delivered from a micro-burette. *Method.*—0·05 to 0·15 g. of the nitrate, containing not more than 0·1 g. of the nitrate ion, are weighed into a 150-ml. flask and dissolved in 10 ml. of water. After addition of 3 ml. of conc. sulphuric acid the solution is cooled and a further 37 ml. of sulphuric acid are added slowly. The liquid is again cooled, and 1 g. of sodium carbonate is added, in portions, with shaking, to remove the dissolved oxygen. When effervescence has almost ceased, ferrous sulphate solution (28 g. of ferrous sulphate in a cooled mixture of 10 ml. of conc. sulphuric acid and 50 ml. of water, diluted to 100 ml.) is added, drop by drop, from a 3-ml. micro-burette. During the titration the liquid becomes yellowish-green; the colour-change at the end-point is to pale pink. One ml. of the ferrous sulphate solution ≡ 0·0310 g. of NO_3. At the end of the titration it is necessary to wait for 3 minutes before reading the burette, to avoid drainage errors. The end-point colour should be matched against that in a comparison tube. Excellent results are obtained and no empirical correction is required, as with the 0·1 *N* ferrous sulphate titration. J. W. M.

Test for Thiourea. E. Storfer. (*Mikrochimica Acta*, 1937, 260–263.)—The reaction between copper salts and thiourea is used for the detection of the latter, especially for the analysis of synthetic resins. *Method.*—The sample (solid, liquid or resinous) is boiled for 2 to 4 minutes with a little water, a small amount of cuprous chloride or other copper salt is added, the mixture is boiled for 1 minute longer, and the clear filtrate is placed on filter-paper impregnated with potassium ferricyanide. A blue or blue-violet fleck indicates that the test is positive. Occasionally, aqueous alcohol or a water-acetone mixture gives better results than water. The limit of identification is 10γ, so that even a resin that is not a pure thiourea resin is easily detected. It is best first to digest the resin with an alkali hydroxide solution containing alcohol or acetone, whereby the combined aldehyde (by the destruction of the methylol or methylene group) is liberated. The solution obtained must be carefully neutralised, as in alkaline solution the thiourea cuprous chloride is decomposed, with the formation of copper sulphide. The further treatment is the same as described above. J. W. M.

Microchemical Colorimetric *p*H Procedure for Differentiating the Telia of *Cronartium ribicola* and *C. occidentale*. R. J. Acree and W. H. Ross. (*J. Agric. Res.*, 1937, 55, 347–352.)—Efficient control of the white-pine blister rust is dependent upon early recognition of advanced infections on ribs. The established methods of species identification failed to furnish means of differentiating *Cronartium ribicola* and *C. occidentale* in the telial stage. Studies involving *p*H reactions showed minute differences, and by certain treatments with acid, distilled water and bromothymol blue under *p*H control gave different colours. *Detail.*—(1) The samples of leaves are placed, telia-bearing surfaces down, in watch-glasses containing 2 ml. of 0·1 *N* hydrochloric acid, and a note is taken of the time. (2) Under the dissecting microscope the samples are reversed, air-bubbles are brushed off with a camel-hair brush, and the samples are turned back again. The watch-glasses are agitated twice. (3) At 20 and 27 minutes from starting-time the watch-glasses are again agitated. (4) After 30 minutes from starting-time the samples are removed with forceps, touched with filter-paper, placed in 50 ml. of water, touched with filter-paper, and then shaken in a jar with 25 ml. of water. (5) After 45 minutes the samples are again shaken and removed to a similar jar with 25 ml. of wash-water. (6) One hour from starting-time the samples are shaken and removed to slides in focus under the dissecting microscope. Excess of water is removed with filter-paper, and the telia are removed from the leaf with a scalpel. About a dozen are placed in the centre of each slide, and enough bromothymol blue (*p*H 7·6) is placed on each lot of telia to make a film between the slide and cover-glass of about the thickness of the telia. The slides are covered and compared under a comparison microscope. After 5 to 15 minutes the yellow colour first formed becomes blue with *Cronartium ribicola* and green with *C. occidentale*. When the maximum colour is attained the indicator is drawn off quickly with filter-paper, and the cover-glass is firmly pressed down on the telia by means of spring clothes' pegs for about 30 minutes or more, and the preparation is examined. J. W. M.

Rapid Micro-method for Determination of Magnesium in Human Milk. M. Hasegawa. (*Tohoku J. Exp. Med.*, 1937, 31, 422–425.)—Magnesium is determined in 1 ml. of human milk by the hydroxyquinoline method, without preliminary removal of calcium, with an average error of ±2·2 per cent. *Reagents.*—(1) De-proteinising agent: 6 g. of sodium tungstate and 15·9 g. of anhydrouf sodium sulphate dissolved in 1 litre of water. (2) 0·33 *N*-Sulphuric acid. (3) Alcoholic 8-hydroxyquinoline solution: 5 g. of 8-hydroxyquinoline in 100 ml. os 95 per cent. alcohol. (4) Concentrated ammonium hydroxide. (5) Powdered ammonium chloride. (6) *N*-Hydrochloric acid. (7) 5 Per cent. ammonium acetate solution. Add a few ml. of (4) to this to render it just alkaline to phenolphthalein. (8) 0·01 *N*-Potassium bromate. (9) Pure potassium bromide. (10) Pure potassium iodide. (11) 0·01 *N*-Sodium thiosulphate standardised each day against (8). (12) 0·25 Per cent. starch solution. *Method.*—Precipitate proteins from 1 ml. of the milk with 8 ml. of tungstate solution and 1 ml. of 0·33 *N*-Sulphuric acid. Stir, and filter after 20 minutes. To 5 ml. of the filtrate in a centrifuge tube add 0·3 to 0·59 ml. of ammonium chloride solution, place in a water-bath at 80° C., and gradually heat to 100° C.; then add 10 drops of ammonia and 10 drops of hydroxyquinoline reagent, and stir until turbid. Leave for 10 minutes on the water-bath, adding one drop of ammonia every 3 minutes to keep the solution alkaline. Centrifuge while hot and wash 3 times with a few ml. of warm ammoniacal ammonium acetate solution (reagent 7). Dissolve the precipitate by warming in 5 ml. of *N*-hydrochloric acid, add 2 or 3 ml. of 0·01 *N*-potassium bromate solution and a little potassium bromide, and close the flask with a stopper. After 3 to 5 minutes add a little potassium iodide and titrate with thiosulphate. J. W. M.

Colour Reaction for Molybdenum with 2:2′-Dipyridyl. A. S. Komarowsky and N. S. Poluektoff. (*Mikrochimica Acta*, 1937, 1, 264–266.)—*Reagents.*—A 3 per cent. solution of 2:2′-dipyridyl in alcohol and a stannous chloride solution (10 g. $SnCl_2$ in 20 ml. of conc. hydrochloric acid). *Method.*—The neutral or slightly acid test solution is treated in a porcelain micro-crucible with 2 drops of 2:2′-dipyridyl solution followed by a drop of stannous chloride solution. In the presence of molybdenum an intense red-violet colour appears, or a precipitate when large amounts are present. The limit of identification is 0·4γ of molybdenum, and the concentration limit 1 in 100,000. Neither rhenium, vanadium nor quinquevalent arsenic gives this reaction. Tungstates interfere, owing to the tungsten blue formed in the reduction; this interference may be prevented by the addition of tartaric acid, when a complex is formed which does not react with stannous chloride. By adding to 1 drop of the tungstate-containing solution 1 drop of 2 *N* tartaric acid solution, 5 to 6 drops of 3 per cent. alcoholic 2:2′-dipyridyl solution and 1 drop of stannous chloride solution, it is possible to detect 0·8γ of molybdenum in the presence of 550 times this amount of tungsten. Experiments to apply this reaction quantitatively are in progress. J. W. M.

Physical Methods, Apparatus, etc.

Fluorescence Microscopy. M. Haitinger. (*Chem.-Ztg.*, 1937, **61**, 847–848.)—A general description of the method and its applications is given. An arc struck between metal electrodes is preferable to the usual mercury vapour lamp as the source of ultra-violet light, as the former gives a brilliant point-source, and the author has obtained successful results with iron electrodes. The fluorescence normally produced by an object when examined under the microscope in such radiations is known as the "primary" fluorescence, but by treating the preparation with certain substances known as "fluorochromes" (which include acids, alkalis and plant extracts) a "secondary" or "induced" fluorescence may be produced, which frequently renders visible additional diagnostic characteristics. Solutions of fluorochromes should be very dilute (*e.g.* preferably 1 mg. in 10 to 1000 ml. of water or 50 per cent. alcohol), and staining takes place rapidly if the specimens are simply immersed in them. The technique is therefore simpler than that required for microscopy in visible light. The objects may easily be photographed in black-and-white, but reproduction in colour is tedious and expensive. Applications of the method which are mentioned include the identification of cell nuclei, fats, sinews, mucous and connective tissue in physiological specimens, and of protein crystals, plasma, and lignin in plant substances. The method has also applications in medicine, pharmacy and the study of fibres. For example, filter-passing viruses and drugs present in the human body are rendered visible (*cf.* Haitinger and others, *Z. Mikros.-Anatom. Forsch.*, 1933, **33**, 194; *Beihefte. Bot. Zentr.*, 1933, **50**, 432; 1935, **53**, 378, 387; *Mikrochem.*, 1935, **16**, 331). J. G.

Testing by Fluorescence. J. A. Radley. (*J. Soc. Dyers and Col.*, 1937, **53**, 376–379.)—Methods and technique are reviewed, with special reference to the textile industries, and examples referring to the examination of raw materials, the detection of faults, and the identification of the constituents of mixtures (*e.g.* dressings) are discussed. Apparent contradictions in the literature of the subject arise from the differences in final treatment which rayons of the same type frequently undergo, and which affect their fluorescence. If viscose rayon is dipped for a few seconds in a hot solution of acronol yellow-TS, and then rinsed and dried, it acquires a brilliant golden-yellow fluorescence which easily distinguishes it from the bright blue-green fluorescence of cellulose acetate rayon when treated by the same process. After cotton has been immersed in a 0·5 per cent. solution of 8-hydroxyquinoline sulphate and then washed and dipped in 5 per cent. sodium hydroxide solution it has a bright violet fluorescence, whilst linen appears canary-yellow. The method can seldom be used to identify dyestuffs on the fibre, as the manner in which oxidation is carried out may exert an important influence. Many benzene substitution products and azo-compounds containing a benzene nucleus are non-fluorescent, although the corresponding naphthalene compounds fluoresce strongly. The NO_2-group and sometimes the OH-group, depresses the fluorescence of the compound into which it is introduced, although in the latter class of compounds the formation of an alkali salt increases the fluorescence again. The only fluorescent nitro dyes are azo dyes obtained by diazotisation and coupling with compounds which are themselves fluorescent. Spoilage due to mineral oil on heavily-dyed fabrics is not easily seen in ultra-violet light, but may be detected by placing the sample on top of a piece of clean white cloth and spotting it with ether, when the oil is carried through to the cloth underneath and may then easily be detected by means of its fluorescence. Similarly, spotting with a non-fluorescent solvent serves to spread out the oil from a spot which is non-fluorescent because of the large quantities of dirt present, and so renders its fluorescence visible. Highly fluorescent substances are sometimes added to printing pastes which are then applied in the light of an ultra-violet lamp, so that defects are easily visible; this is of special use for colours which are printed in the first instance as almost colourless pastes (*e.g.* Soledon dyes). Metallic compounds in dressings are detected by evaporating an extract of the cloth in boiling water to about one-half of its original bulk and then adding alcohol to precipitate any starch; the mixture is filtered, the filtrate is concentrated, and fluorescence tests are applied. Examples are the cochineal reagent for boric acid, the urobilin test for zinc, the 8-hydroxyquinoline test for zinc or magnesium, and the tetrahydroxyflavonol (morin) reagent for aluminium. Tests for soaps, pigments, synthetic resins, albumen and casein are also dealt with. J. G.

Air Conditioning. Ventilation Conditions and their Investigation. R. C. Frederick. (*Proc. Roy. Soc. Med.*, 1937, **30**, 1541–1543.)—A determination of the carbon dioxide content of the air in a room (*e.g.* by the Haldane method) provides a reliable indication of the degree of respiratory impurity. For healthy conditions a maximum quantity of 12 p.p. 10,000 has been suggested, but 9 parts is considered by the author to be a more suitable figure; this quantity, however, is only an index and is quite harmless, detrimental effects being appreciable only when more than 300 p.p. 10,000 are present. So long as the oxygen-content is not less than 17·5 per cent. the amount present is without physiological importance, and an actual determination is seldom necessary; it may, however, be made by the Haldane method, or by multiplying the carbon dioxide figure by 1·1 and subtracting the resulting figure from 20·95. The air-supply is measured most accurately by means of a Pitot tube attached to a slope gauge or a differential liquid gauge, though the recently-introduced Alnor velometer is preferable if an immediate reading in feet per minute is required; a figure of 2000 to 3000 cb. ft. per man per hour is desirable, but adequate floor-space is equally important. Optimum dry-bulb temperatures (in °F.) are: for hard work 60 to 62, for sedentary work 62 to 64, and for leisure 64 to 66, in each instance with a relative humidity of 70 to 75 per cent. The author considers that Haldane's limits for wet-bulb temperatures—in still air 88° F. for sedentary work and 78° F. for hard work; in moving air 93° F. for sedentary work and 85° F. for hard work—could be placed higher. Comfort also depends upon the cooling power of the air (or heat-loss from the body), and this is determined by the katathermometer in millicalories per sq. cm. per second. A dry and wet kata of 5 and 15 respectively are considered preferable to the standards promulgated (6 and 18); under tropical conditions a wet kata of 10 should be the aim, but 8 can scarcely be regarded as unsatisfactory.

The combined effect of dry- and wet-bulb temperatures, relative humidity and air-movement is known as the "effective temperature." Thus, an effective temperature of 65° F. is the equivalent of saturated motionless air at 65° F., and other effective temperatures may be deduced from a chart (not published in the original paper) relating these variables. This chart contains a "comfort zone" which, however, is at present applicable only to conditions in America. J. G.

Reviews

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Fourth Edition. Volume I, A—Bi. By J. F. THORPE, C.B.E., D.Sc., F.R.S., and M. A. WHITELEY, D.Sc., F.I.C. Pp. 703. London: Longmans, Green & Co. 1937. Price 63s.

The advent of a new edition of Thorpe's Dictionary is quite an event in the chemical world. Such is the established reputation of the work that it is the first to which the industrial chemist turns when he has a new problem to solve; he seldom looks in vain and nearly always finds something helpful with references to further sources of information. Obviously, to retain such a foremost position the Dictionary must be kept up-to-date; to do this is no easy matter, having regard to the magnitude and rapid growth of the subjects included under the term Applied Chemistry to-day. The third edition was complete in 1927, and in 1934–36 there appeared a two-volume supplement and an index with glossary. Supplements, useful as they are, are not an entirely satisfactory means for keeping up-to-date an encyclopaedia such as this Dictionary really is. So the Editors have very wisely decided to start afresh and provide completely new matter. This is to be done at the rate of one volume per year; and, as this involves a prolonged period, they have devised a plan whereby each succeeding volume will be used for bringing the earlier ones up-to-date. Each item of importance contained in an earlier volume will be dealt with under its own initial letter and any up-to-date additions included. For example, material having an initial letter A included in a general article O will now be described under A and brought up-to-date under the letter O; or matter having initial letter H, described in a general article under B, will be mentioned again in the volume containing letter H. We shall observe with interest how this ingenious device works out in practice.

The publishers of the Dictionary are to be warmly congratulated on the set-up of the text with its sometimes complex formulae, and upon the binding. The covering material used has been dyed with Monastral Blue, which is peculiarly appropriate, for the production of this unique pigment—which is superior to all other colours in respect of fastness to light, acids and alkalis—is generally regarded as the greatest chemical achievement of the year 1936.

The increase in size of the work is illustrated by the fact that Volume I now covers A to Bi, as compared with A to Calcium in the third edition. It is the work of some seventy-five contributors, all the names in the list being those well known in their respective fields, affording proof that the articles for which they are responsible is authoritative. The Editors have welded such a long list of authors and subjects with much skill and no discordant styles are to be found. Among the major changes noted in the subject-matter of the first volume is the omission of the excellent 100-page article on Analysis by Sir Gilbert Morgan, and of 50 pages on Azo dyes; it is understood that the former will be replaced by an extended article from the same versatile pen under the heading of Chemical Analysis. Azo dyes are to appear under Dyestuffs. Notwithstanding the saving of 150 pages on these two articles, Volume I only reaches the end of Bi. This is mainly due to the inclusion of many new small entries and to the extension of all the major articles by 50 to 100 per cent. There are, however, some major new ones such as Absorption (4 pages); Acetaldehyde (18 pages), by Dr. Farmer; Ageing, by Dr. Jordan; Alloys, Light, by F. Horn; Anthraquinone and its Dyestuffs (40 pages), by Drs. Goldsberg and Fraser Thomson; Atomic Structure (7 pages), by Dr. Emeléus. Many other articles are notably increased, which is a proper result of their increased technical importance. The derivatives of Acetylene, which form the basis of a great industry, require 45 pages where 20 used to suffice; organic arsenicals occupy 18 pages, against the former 10, and autoclaves now require 10 pages, whereas a few years ago one page sufficed. The article on Balance now includes a concise description of Conrady's method of weighing; barbituric acid and the barbiturates, too, are given space more commensurate with the study and use they have lately received.

It will be realised that no one person can possibly appraise the value of all parts of so great a work as this Dictionary. The reviewer has tested it in two ways: first by reading several of the articles and noting that they are really up-to-date, and secondly, by consulting the volume on each problem which has come along recently; it was always found to be helpful. The standard of excellence which Thorpe's Dictionary has long enjoyed is maintained, even enhanced, by the first volume of its new edition. The Editors have shown their courage and industry in undertaking such an immense task, and both they and their contributors are to be congratulated on the skill with which the first part has been accomplished.

H. E. Cox

SILICATE ANALYSIS. By A. W. GROVES, D.Sc., Ph.D. Pp. xxi + 230. London: Murby & Co. 1937. Price 12s. 6d. net.

This book should be welcomed as a further step towards the co-operation between geologists and chemists which is so essential if a high standard in the analysis of rocks and silicate minerals is to be attained. The author stresses the fact that complete and detailed analyses are necessary to the geologist and emphasises the importance of the determination of such constituents as carbon dioxide, barium, strontium, fluorine, sulphur, and so on, in addition to those usually determined. The limitations of analytical methods are described in such a manner that the geologist will be able to obtain a clear idea of the problems confronting the analytical chemist and the difficulties met with in rock analysis.

The first two chapters deal with laboratory equipment, apparatus and reagents, and the author evidently considers that elementary advice is worthy of inclusion, possibly for the benefit of geologists with little analytical training. A few notes on the preparation of solutions of indicators, together with the *p*H values of their transition-ranges, might have added to the usefulness of the chapter on reagents.

Sampling is dealt with in a brief but adequate manner, and the preparation of the sample for analysis is clearly described. Some 100 pages devoted to analytical methods are preceded by a useful discussion on the constituents to be determined and a short chapter on "Common Operations," containing much useful advice. It is doubtful if the author is correct in suggesting the use of sulphuric acid as a desiccating agent in balance-cases, even when "all metal parts of the balance are lacquered." Hillebrand and Lundell consider that desiccating agents in balance-cases are of little value under normal conditions, and assert that sulphuric acid should never be used.

In the chapters devoted to analytical methods a general account of the principles involved is followed, in each instance, by a full account of the various analytical procedures. The close attention paid to details is highly commendable, and it is obvious that the author has had first-hand experience of the methods. The methods described are, in general, well known and accepted as the most accurate and reliable. In some of them modifications have been introduced which are claimed to be improvements, and a few new methods are included, notably the author's own method for copper and that of Knowles for beryllia.

The author is in agreement with Hillebrand and Lundell as to the limits allowed for the summation of a rock analysis, and his contention that an analysis with a summation less than 99·75 per cent. indicates undetermined constituents is sound. The limits of error suggested for individual constituents represent a high standard of work, but one that is not unattainable provided that pure reagents and an ample supply of platinum are available.

In Chapter XI the author is evidently on very familiar ground and gives a valuable account of the distribution of the elements, with numerous references to recent work, which should be of great interest to the chemist. Recent work on X-ray investigations into the structure of minerals is referred to in the following chapter, and the use of general formulae obtained in this way as a check on the accuracy of the chemical analysis is described. The use of the geological "norm" as a check on the analysis of rocks is not quite so clear.

Considering the scope of the book, the errors are few. On page 64 an excessive amount of diammonium phosphate (1 to 3 grams) is used in the second precipitation for magnesium, and on page 115 "excess silica" is precipitated as silver chloride by the addition of sodium chloride. Conservative tendencies are shown by the use of the "c.c." throughout the book and the lack of references to micro-chemical work. These could have been introduced with advantage in the notes on "Mineral residues from human silicotic lungs."

"Silicate Analysis" is essentially a laboratory handbook which should prove of value to all geologists and chemists interested in the analysis of rocks. A. SHAW

BIOLOGICAL LABORATORY TECHNIQUE. By J. BRONTË GATENBY, M.A., Ph.D., D.Sc. Pp. 130. London: J. & A. Churchill, Ltd. 1937. Price 7s. 6d.

This little book, as essentially practical in nature as its title suggests, was designed primarily for teachers and students of biology and for amateur naturalists —a rather maligned group of men to whom biological science the world over owes an enormous debt.

Analysts as such must always be interested in manipulative laboratory methods, even when these are somewhat removed from humdrum estimations of arsenic and determinations of freezing-points. This book is likely to provide them with information that is useful as well as interesting, for there are many analysts who have on occasion to examine microscopically the tissues of live or newly dead plants or animals. For these, Professor Gatenby has most usefully put his immense experience into black and white, and there will be few microscope users who can fail to gain knowledge and skill from considering his descriptions of staining and smear technique, and of methods of fixing, mounting and embedding.

The book contains a number of useful semi-diagrammatic illustrations, is clearly printed and laid out, and is probably destined in the hands of the user, through continuous life on his microscope bench, rapidly to acquire a cover as multi-coloured as Joseph's. A. L. BACHARACH

TEXT-BOOK OF PHARMACEUTICS. By A. O. BENTLEY, Ph.D. Fourth Edition. Pp. xii + 1022. With Appendix and 250 illustrations. London: Baillière, Tindall & Cox. Price 15s.

When a text-book has reached the stage at which a fourth edition is demanded it is evident that it has filled a specific need. In modern pharmacy so many changes have been made during the past decade, that it is not sufficient to revise a book dealing with Pharmaceutics, but also necessary to add entirely new sections.

The comprehensive title of this book permits or compels the author to include so much information entirely new to the practice of pharmacy of half a century ago, that the opening three chapters are very suitably devoted to historical details, the causes for the founding of the Pharmaceutical Society, and the development of the present British Pharmacopoeia, from its previous five editions; most of this is of importance to analysts concerned in work under current official regulations.

The author has interspersed the chapters dealing with the elementary principles of pharmacy with the recent scientific explanations of many things that were done by rule of thumb or trained dexterity, fifty years ago.

Chapters in the book on Osmotic Pressure, Electrolysis, Hydrogen Ion Concentration, and Adsorption, have been contributed by Dr. J. B. Firth, and will be appreciated as much by qualified men as by advanced students.

Mr. H. A. Turner has written most useful chapters on Isotonic Solutions and the Theory of Emulsions, and Dr. H. S. Holden has dealt at length and with great lucidity on the Enzymes (and their effects) in the substances employed in medicine.

The chapters dealing with the purely pharmaceutical methods for the preparation of drugs for use in medicine are as complete in detail as is possible in a work which does not claim to be a text-book on Materia Medica.

The biology of bacteria, the sterilisation of fluids for hypodermic use, and of surgical dressings, and the methods of preparing and filling ampoules, are subjects of particular interest to analysts whose practice includes such work.

Vaccines and Sera for the treatment of pathological conditions form an important department of medical practice and pharmacy, and the inclusion in the British Pharmacopoeia and its recent supplement of so many types of these aids to the treatment of disease, makes such a chapter of vital importance to the pharmaceutical graduate of to-day.

Part VI of the book deals with the biological assay of pharmaceutical preparations, the testing of Insulin, Digitalis and Strophanthus, Arsphenamine Compounds, Pituitary, Toxins, and Antitoxins. This section has been compiled by Mr. W. A. Broom, and gives in thirty pages a whole compendium of the subject in a readable but correctly stated exposition of these new subjects.

The book is very well printed and illustrated, for critical examination could detect but few printer's errors, and it is hardly fair to ask the author how to scrape hydrogen carbonate, after being told on page 725 that it is not necessary to do so; or to enquire how Calamine can be prepared by elutriation from the native zinc carbonate when the mineral is unobtainable. Only a practical laboratory hand could produce Confection of Senna by the method given on page 622, and then only by considerable modification of the abbreviated directions.

C. EDWARD SAGE

FLUORINE INTOXICATION. A CLINICAL HYGIENIC STUDY WITH A REVIEW OF THE LITERATURE AND SOME EXPERIMENTAL INVESTIGATIONS. By KAJ ROHOLM. Pp. 364. With 96 illustrations. Copenhagen: Arnold Busck. London: H. K. Lewis & Co., Ltd. 1937. Price 20s. net.

This book gives the results of a detailed study, chiefly from the medical viewpoint, of fluorine poisoning in its various forms, more particularly the osteosclerosis affecting workers in a Copenhagen cryolite factory. The subject-matter is dealt with under four main headings: a general review of the effects of fluorides on man, animals and plants; investigations into industrial cryolite poisoning; an account of experiments on animals, and a part devoted to discussion and general conclusions.

The effect of fluorides in producing more or less severe bone affections (osteomalacia) in cattle and other animals has been known for about forty years, but it is only recently that chronic fluorine poisoning in man has been recognised, in its more severe form as osteosclerosis, and in the milder form as an affection of dental enamel, known as "mottled teeth."

Cases of mottled teeth occur in many places in the United States, in South America, in North Africa, in several European countries, and in China and Japan. In this country they occur at Maldon in Essex, where the public water supply contains 5 parts of fluorine per million. A similar condition is prevalent among sheep in North Africa due to fluorides in the soil. In Iceland, after volcanic eruptions, the surface soil and grass are so heavily contaminated with fluoric dust that there is actually a heavy mortality among sheep. In Icelandic literature from about the year 1000 up to recent times there are repeated references to the disastrous effect of volcanic dust on domestic animals.

The author discusses a number of other possible sources of chronic fluorine poisoning in man, which, although they have not actually been shown to be responsible for definite symptoms, must, in the light of recent knowledge, be regarded with suspicion. It is not so very long ago that fluorides and fluosilicates were widely recommended as non-toxic preservatives for food. Cryolite, barium fluosilicate and other fluorides are being widely used as agricultural insecticides on vegetables and fruit. Rock phosphate containing 3 or 4 per cent. of fluorine is used for the manufacture of superphosphate, and many thousands of tons of fluorides are thus applied annually to the soil and may conceivably be taken up by crops.

The analytical side of the fluorine question is not accorded the same exhaustive treatment as the medical side. In 360 pages only four are devoted to analytical technique, a subject which the author considers to be outside the scope of his enquiry in what is primarily a medical work.

The translation of the book from the original Danish, undertaken by W. E. Calvert, of Copenhagen, has been admirably done, except perhaps in the short analytical section, which shows a lack of familiarity with analytical technique. There are very few misprints, a matter upon which the Danish printers are to be congratulated.

The book is illustrated by a number of excellent photographs of the effects of fluorine on bones and teeth. It has one serious defect as a work of reference—there is no index, and the table of contents at the beginning is not sufficiently detailed to compensate for this omission.

There is a complete bibliography with references to nearly 900 original papers.

G. W. MONIER-WILLIAMS

A TEXT-BOOK OF QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR I. VOGEL, D.Sc., D.I.C., F.I.C. Pp. 383. London: Longmans, Green & Co. 1937. Price 7s. 6d.

This book falls in the class ranging between elementary introductions to qualitative analysis and the full-dress text-book with claims to exhaustive treatment; in this class it will, without doubt, take a high place. Judged as a whole, it is a very creditable production.

The general lay-out of the practical part follows traditional procedure, so that anyone who has completed an inorganic qualitative course will be able to follow it without need of the index. The author's share in the production is his critical selection of the subject-matter and the lucidity with which it is presented. The success of the book should be assured by the skill with which he has incorporated so much of the best of recent theory and practice without any disturbance to the ancient landmarks.

The work has been well done; it is written in lucid, easy style, ably backed by the publisher and printer with good paper, clear print and comparative freedom from typographical error. The binding, however, does not compare well with some of the same publishers' other chemical publications, and is not likely to last for long on a laboratory bench; yet if the price is taken into consideration, this is, perhaps, a matter of minor importance.

The book is divided into seven sections. (1) Theoretical (98 pages), to which the author draws attention in his preface, covers everything bearing on the subject from Ostwald to Sørensen, with the exception of the theory of coloured metallic co-ordination compounds. It shows evidence of severe condensation, but has lost nothing in clarity, and finds space for frequent reference to practical applications. (2) Analytical Operations (149 pages) consists of a short but sufficient section on laboratory manipulation. In (3), Reactions of Ions, the treatment is very full, with constant back-reference to the theoretical section. In addition to all the usual reactions and dry tests, twenty organic reagents are described, and also made use of in some of the group separations. Emphasis is laid on the necessity for controlled hydrogen ion concentration for the precipitation of sulphides, and details of the adjustment are described. The sensitivities of the more important reactions, and the solubilities of the precipitates are given in the text; these, together with the author's comments and criticisms of reactions and methods of manipulation, render the section one of the most valuable in the book. (4) Systematic Inorganic Analysis occupies fifty-seven pages, and (5) Modifications of Procedure in presence of interfering inorganic and organic acid radicals, 13 pages. The separation tables are, for the most part, on classical lines, and are preceded by dry tests. The lay-out is clear and easy to follow. The author has taken great pains with "phosphate separations." Five methods are described with a clarity that should go far to remove initial difficulty from a separation that demands care even from the experienced, and is a confusing problem to a beginner.

Throughout the tables of separation the term "residue" is used for material precipitated by a reagent as well as for that which remains after treating a partially soluble mixture with a selective solvent. With two words available, each having a separate and useful signification, the reviewer suggests that it would be better to preserve the distinction, rather than make one do double duty.

(6) "The Rarer Elements," covered briefly in 13 pages, are treated separately and not included in the routine group separation tables, where most of them first attract attention in actual practice. A note in the tables, with a cross-reference to the special section, seems advisable.

It would not be difficult to make out a good case for the suppression of the distinction "rare" as applied to the elements treated, or to some not included. From a student's point of view, the best criterion of rarity is the liability of an element to appear in an examination for which he is preparing. Is it unfair to suggest that if a particular element has been set in such an examination, within recent years, it has ceased to be rare? If this argument is admitted, most of the elements in the "rare" section should be transferred to, and treated in, the systematic part; and at least one more should be added. These remarks apply to the Institute of Chemistry's examination for the Associateship, for which the preface claims that the book provides a suitable course.

Gold and platinum are classed as "rarer elements," whereas Valentin (1880) placed them, without comment, in their analytical group. There seems to be some confusion here between rarity imposed by Nature and scarcity created by artificial means.

(7) An appendix (29 pages) contains the usual tables, suggested courses of instruction, model analyses and instructions for the preparation of test solutions of known ionic strength. These solutions are recommended in order that students may be encouraged to acquire the ability to judge the relative proportions of the constituents present in a mixture from the volumes of precipitates obtained.

Three self-evident misprints were noted (pp. 87, 131 and 272), and one error (p. 276), where stannic compounds are included amongst those reduced by sulphurous acid.

F. L. OKELL

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A HUNDRED YEARS OF CHEMISTRY. By A. FINDLAY. Pp. vii + 352. London: Duckworth & Co. 1937. Price 15s. net.

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